Quantum Mechanics

THEORY AND APPLICATIONS

Third Edition

A. K. Ghatak
S. Lokanathan

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QUANTUM MECHANICS

> *I cannot tell how the truth may be*
> *I say the tale as it was said to me*
>
> **Sir Walter Scott**

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Quantum Mechanics: Theory and Applications

Third Edition

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First Edition, 1975
Second Edition, 1977
Reprinted 1979 (twice), 1981, 1982, 1985

Third completely revised edition, 1984 by
MACMILLAN INDIA LIMITED
DELHI BOMBAY MADRAS BANGALORE
HYDERABAD LUCKNOW PATNA
TRIVANDRUM

Associated companies throughout the world

SBN 33390 456 7

Published by S. G. Wasani for Macmillan India Limited
2/10 Ansari Road, Darya Ganj, New Delhi, 110 002

Printed by :
Pushp Print Services, Maujpur Shahdara, Delhi-53

To our teachers
Professor H A Bethe
Professor D S Kothari
Professor R C Majumdar
Professor R Serber

To our teachers

Professor H A Bethe

Professor [illegible]

Professor [illegible]

Professor [illegible]

Preface

Quantum Mechanics has long been recognized as an essential ingredient in the training of a physicist at an early stage in his studies. No matter which specialization the student chooses in his later career, it is necessary for him to develop not merely an understanding of the basic principles of Quantum Mechanics but an ability to apply these principles in his field.

Textbooks on Quantum Mechanics addressed to students at graduate and post-graduate levels generally have few solved problems; moreover, the problems suggested are largely of an academic nature with a greater emphasis on theory than on applications. This book attempts to present a more balanced account of these two aspects and has evolved from lectures given by the authors at the Indian Institute of Technology, New Delhi and at University of Rajasthan, Jaipur. The emphasis has not been on rigour but on making results plausible and helping the student to become familiar with methods for solving problems.

Each chapter gives a concise account of the theoretical principles followed by a number of problems. The problems have been chosen to present a fair amount of diversity in applications. The solutions to most of these problems are given at the end of each chapter. This will enable the student to refer to the solutions when necessary and at the same time provide him an opportunity, if he so wishes, to solve some or all of these problems by himself before consulting the solutions.

We have given a somewhat lengthy account of the Dirac notation of bras and kets; since this is used frequently in advanced work, it was felt that the student would benefit greatly if he became familiar with it right at the beginning.

We have dedicated this book to Professor H. A. Bethe who taught one of us (AKG) at Cornell, to Professor R. Serber who taught the other (SL) at Columbia, and to Professors D. S. Kothari and R. C. Majumdar who taught both of us at Delhi University. These teachers were responsible for stimulating our interest in Quantum Mechanics.

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Acknowledgements

We are indebted to Elsevier Publishing Co., Amsterdam for permission to reproduce the Nobel lectures and to Addison Wesley Publishing Co., Reading; McGraw-Hill Book Co., New York; Oliver and Boyd Ltd., Edinburgh; Oxford University Press, Oxford; Penguin Books Ltd., Middlesex and Prentice Hall Inc., Englewood Cliffs for permission to adapt figures, tables and treatments from the following books.

G. Baym, *Lectures on Quantum Mechanics*, Addison Wesley (1969).
P. A. M. Dirac, *Quantum Mechanics*, Oxford University Press (1958).
H. Enge, *Introduction to Nuclear Physics*, Addison Wesley (1966),
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We would also like to express our deep sense of gratitude to Dr. K. Thyagarajan and Dr. B. P. Pal for their continual help and numerous suggestions. Special thanks are also due to Dr. Enakshi Sharma, Dr. Anurag Sharma, Dr. Arun Kumar, Dr. U. Jain and Mr. S. I. Hosain for numerous suggestions and continuous help in bringing out the book in its present form and to Prof. S. C. Mathur, Dr. B. K. Sharma and Dr. K. B. Bhalla for their valuable suggestions. To Mr. M. R. Shenoy and Mr. R. N. Tewari we extend our thanks for helping in the tedious task of proof-reading. We are also grateful to Prof. M. S. Sodha for his encouragement in this endeavour.

Finally, it would be inappropriate if we did not thank our wives, Gopa Ghatak and Amrutha Lokanathan for their patience and understanding.

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Physical Constants

C = coulomb; esu = electrostatic units;
eV = electron volt; F = farad; G = gauss;
H = henry; Hz = hertz = cycles/s; J = joule;
K = kelvin (degree Kelvin); m = meter; N = newton;
s = second; T = tesla

Digits in parenthesis following each quoted value represent the standard deviation error in the final digits of the quoted value; e.g. 6.626176 (36) implies 6.626176 ± 0.000036, etc. Most of the quoted values are taken from 'The 1973 Least-Squares Adjustment of the Fundamental Constants' by E. R. Cohen and B. N. Taylor, *J. Phys. Chem. Ref. Data*, Vol. 2, No. 4, pp. 663-734, 1973.

Conversion Factors

1 N = 10^5 dynes
1 J = 10^7 ergs
1 eV = 1.6021892 (46) $\times 10^{-19}$J
1 C = 1 amp. s = 2.997924580 (12) $\times 10^9$ esu
1 T = 1 weber. $m^{-2} = 10^4$ G
1 F = 1 $C^2. N^{-1}. m^{-1}$
1 H = 1 weber. amp^{-1} = 1 $N.m.s^2. C^{-2}$
1 Electron mass ($= m_ec^2$) = 0.5110034 (14) MeV
1 Proton mass ($= m_pc^2$) = 938.2796 (27) MeV
1 Neutron mass ($= m_nc^2$) = 939.5731 (27) MeV
1 atomic mass unit ($= uc^2$) = 931.5016 (26) MeV
(u = atomic mass unit in the unified atomic mass scale $^{12}C = 12$)

Quantity	*Symbol*	*Value*	*Uncertainty (parts per million)*
Speed of light in vacuum	c	2.997924580 (12) $\times 10^8$ m $\cdot$ s^{-1}	0.004
Planck's constant	h	6.626176 (36) $\times 10^{-34}$ J $\cdot$ s	5.4
	$\hbar = h/2\pi$	1.0545887 (57) $\times 10^{-34}$ J $\cdot$ s	5.4
Electronic charge	q (mks)	1.6021892 (46) $\times 10^{-19}$ C	2.9
	e (cgs)	4.803242 (14) $\times 10^{-10}$ esu	2.9
Electron rest mass	m_e	9.109534 (47) $\times 10^{-31}$ kg	5.1

Proton rest mass	m_p	$1.6726485\ (86) \times 10^{-27}$ kg	5.1
Ratio of proton mass to electron mass	m_p/m_e	1836.15152 (70)	0.38
Neutron rest mass	m_n	$1.6749543\ (86) \times 10^{-27}$ kg	5.1
Permeability of vacuum	μ_0	$4\pi\ (= 12.5663706144) \times 10^{-7}$ H.m^{-1}	
Permittivity of vacuum	$\epsilon_0 = 1/\mu_0 c^2$	$8.854187818\ (71) \times 10^{-12}$ F.m^{-1}	0.008
Fine structure constant	$\left.\begin{aligned}\alpha &= q^2/4\pi\epsilon_0 \hbar c \text{ (mks)}\\ &= e^2/\hbar c \text{ (cgs)}\end{aligned}\right\}$	$7.2973506\ (60) \times 10^{-3}$	0.82
		$1/\alpha = 137.03604\ (11)$	0.82
Rydberg constant	$R_\infty = (q^2/4\pi\epsilon_0)^2$		
	$m_e/4\pi\hbar^3 c$ (mks)	$1.097373177\ (83) \times 10^7$ m^{-1}	0.075
	$= m_e e^4/4\pi\hbar^3 c$ (cgs)	$1.097373177\ (83) \times 10^5$ cm^{-1}	0.075
Non-relativistic ionization potential of hydrogen atom with infinite proton mass	$R_\infty hc$	$2.179907\ (12) \times 10^{-18}$ J	5.4
		13.605804 (36) eV	2.6
Rydberg constant for hydrogen	R_H	$1.09677576\ (12) \times 10^7$ m^{-1}	
Bohr radius	$a_0 = (4\pi\epsilon_0\hbar^2)/(m_e q^2)$ (mks)	$5.2917706\ (44) \times 10^{-11}$ m	0.82
	$= \hbar^2/m_e e^2$ (cgs)	$5.2917706\ (44) \times 10^{-9}$ cm	0.82
Bohr magneton	$\mu_B = q\hbar/2m_e$ (mks)	$9.274078\ (36) \times 10^{-24}$ J.T^{-1}	3.9
	$= e\hbar/2m_e c$ (cgs)	$9.274078\ (36) \times 10^{-21}$ erg. G^{-1}	3.9
Electron magnetic moment	$\mu_e\ [= (g_e/2)\mu_B]$	$9.284832\ (36) \times 10^{-24}$ J. T^{-1}	3.9
Free electron g-factor	$g_e = 2\mu_e/\mu_B$	2.0023193134 (70)	0.0035
Nuclear magneton	$\mu_N = q\hbar/2m_p$	$5.050824\ (20) \times 10^{-27}$ J. T^{-1}	3.9
Proton magnetic moment	μ_p	$1.4106171\ (55) \times 10^{-26}$ J. T^{-1}	3.9
Boltzmann constant	k	$1.380662\ (44) \times 10^{-23}$ J. K^{-1}	32
		$0.861734\ (27) \times 10^{-1}$ eV. K^{-1}	31

Chronological Development of Quantum Mechanics: a very Brief Account

The development of quantum mechanics as a unified structure did not take place in the smooth way that is usually presented in a text book. For a text book to present this development in chronological fashion is, however, not really a fruitful way of presenting the subject to the student. On the other hand, we feel that every student ought to have some sense of perspective of this development. As mentioned by Ludwig (1968) 'without taking account of its historical development, an existing theory often appears almost as if it had "fallen from heaven". However, the question of the development of a theory is important not only to satisfy our curiosity but also because much can be learnt from it for the future'. Keeping this in mind we give a very brief account of the chronological development of quantum mechanics highlighting some of the important facts associated with the development and also giving reference to books (which are usually available in most libraries) where some of the original papers have been reprinted. We hope that this introduction will induce the reader to go back to some of the articles written by the 'masters' of the subject so that he is able to get a perspective of the field as it developed.

We should mention that perhaps the most comprehensive account of the chronological development of quantum mechanics is given in the book by Jammer (1966) which has also given detailed references of most of the important publications during the development of the field (and where they could be found). There are numerous other books/articles written on the historical development of the subject, particular reference can be made to Born (1969), Condon (1952), Cropper (1962), Ludwig (1968), Ter Haar (1967). We felt that the Nobel lectures by three of the founding fathers of modern quantum theory (Heisenberg, Schrödinger and Dirac) would convey the excitement of the struggle of ideas presented in a style that no one else can possibly match. We are reminded of the remark made by Lord Rutherford who, when told that he seemed to be riding the crest of the wave, said 'well, I made the wave, didn't I' ! We therefore reproduce the Nobel lectures by people who indeed made the subject; however, before that we give a brief account of the chronological development:

1900: In a paper entitled 'On an improvement of Wien's equation for the Spectrum', Planck "guessed" the blackbody radiation formula (Eq. 5 of Chapter 1) and found that it is in excellent agreement with the experimental data. In a subsequent paper entitled 'On the theory of the energy distribution law of the normal Spectrum' he derived this formula by introducing a drastic assumption that the oscillators can only assume discrete energies. Planck wrote "We consider, however—this is the most essential point of the whole calculation—E to composed of a very definite number of equal parts and use thereto the constant of nature $h = 6.65 \times 10^{-27}$ erg sec. This constant multiplied by the common frequency ν of the resonators gives us the energy element ε in erg . , . . ." The two papers of Planck are reprinted by Ter Haar (1967). It may be of interest to mention that in an unpublished letter to R.W. Wood, Planck wrote [quoted from Jammer (1966)] that the postulate of energy quanta was 'an act of desparation' done because 'a theoretical explanation *had* to be supplied at all cost, whatever the price'. Planck was awarded the 1918 Nobel prize in Physics for his *discovery of energy quanta*; his Nobel lecture was on 'The genesis and present state of development of the quantum theory'.

1905: In a paper entitled 'On a heuristic point of view about the creation and conversion of light' [reprinted in Ter Haar (1967)], Einstein introduced the light quanta. In this paper he wrote that for explanation of phenomena like black-body radiation, production of electrons by ultraviolet light (which is the photoelectric effect) it is necessary to assume that "when a light ray starting from a point is propagated, the energy is not continuously distributed over an increasing volume, but it consists of a finite number of energy quanta, localized in space, which move without being divided and which can be absorbed or emitted only as a whole". Einstein received the 1921 Nobel prize in Physics for his *discovery of the law of photoelectric effect* and *not* for his theory of relativity. It is interesting to note that Einstein did not have the symbol h in his paper; he used the quantity $R\beta\nu/N$ for the energy of the light quanta where R/N and β are actually k and h/k respectively.

1913: In a paper entitled 'On the constitution of atoms and molecules' [reprinted in Ter Haar (1967)], Bohr gave the first successful interpretation of atomic spectra. (The experimental study of atomic spectra was started around 1860 and in 1885 Balmer gave his famous empirical formula which came to be known as Balmer series). His logic of argument was somewhat as follows: For an electron rotating in a circular* orbit around a proton the potential energy is $-e^2/a$, the kinetic energy ($\frac{1}{2}mv^2$) is $e^2/2a$ and therefore the binding energy is given by

$$E_b = e^2/2a$$

The frequency ν' of the orbiting electron is given by

$$\nu' = \frac{v}{2\pi a} = \left(\frac{2E_b}{m}\right)^{1/2} \frac{1}{2\pi} \frac{2E_b}{e^2} = \frac{\sqrt{2}\, E_b^{3/2}}{\pi e^2 m^{1/2}}$$

Bohr than *assumed* that "during the binding of the electron, a homogeneous rediation is emitted of a frequency $\nu = \frac{1}{2}\nu'$; then from Planck's theory, we might expect that the amount of energy emitted by the process considered is equal to $\tau h\nu$, where h is Planck's constant and τ an entire number". Thus

---

*Actually Bohr's consideration was for elliptical orbits; here, for the sake of simplicity we are considering circular orbits.

$$E_b = \tau h\nu = \frac{1}{2}\tau h\nu' = \frac{1}{2}\tau h\left[\left(\frac{2}{m}\right)^{1/2}\frac{E_b^{3/2}}{\pi e^2}\right]$$

which gives

$$E_b = \frac{2\pi^2 me^4}{\tau^2 h^2}$$

and when an atom makes a transition from one stationary state ($\tau = \tau_1$) to another ($\tau = \tau_2$) a light quantum of frequency

$$\frac{2\pi^2 me^4}{h^3}\left[\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right]$$

is emitted. The above formula agreed with the experimental data.

It should be mentioned that the quantization of angular momenta was put forward by Bohr in a subsequent paper in the same year. Bohr was awarded the 1922 Nobel prize in Physics for his *investigation of the structure of atoms, and of the radiation emanating from them*. His Nobel lecture on 'The structure of the atom' gives a good summary of the important results in atomic theory.

1914: In a paper entitled 'On the excitation of 2536 Å mercury resonance line by electron collisions' [reprinted in Ter Haar (1967)], Franck and Hertz showed that by varying the kinetic energies of the electrons hitting an atom it is possible to produce controlled excitation of atoms and molecules; the experiment proved the discrete energy states of atoms, a hypothesis put forward by Bohr in 1913. Franck and Hertz received the 1925 Nobel prize in Physics *for their discovery of the laws governing the impact of an electron upon an atom*.

1917: In a paper entitled 'On the quantum theory of radiation' [reprinted in Barnes (1972), Ter Haar (1967)], Einstein put forward the existence of stimulated emission and introduced the famous A and B coefficients which are now known as the 'Einstein coefficients'.

1922: Stern and Gerlach performed their famous experiment which demonstrated that in the presence of a strong inhomogeneous magnetic field, a beam of silver atoms split into two beamlets. This provided a confirmation of space quantization.

1923: Compton reported his studies on the scattering of X-rays by solid materials (mainly graphite) and showed that the shift of the wavelength of the scattered photon could be explained by assuming the photon having momentum equal to h/λ. Compton shared the 1927 Nobel prize in Physics 'for his discovery of the effect named after him'. The original papers of Compton have been reprinted in a book by Shankland (1973).

1924: In a paper entitled *Investigations on quantum theory* [reprinted in Ludwig (1968)], De Broglie suggested the idea of waves associated with electrons. He recognized that the condition for the kth orbit

$$mv_k r_k = k\hbar$$

implies

$$2\pi r_k = n\,\frac{h}{mv_k} = n\lambda$$

i.e., the circumference of the allowed orbit contains an integral number of wavelengths. He wrote 'in order to have a stable state the length of the channel must be in resonance with the wave'. De Broglie was awarded the 1929 Noble prize in Physics 'for his *discovery of the wave nature of electrons*'.

1925: Pauli in his paper entitled 'On the connection between the completion of electron groups in an atom with the complex structure of spectra' [reprinted in Ter Haar (1967)] put forward the "fourth quantum number of the electron" and the exclusion principle. He was awarded the 1945 Nobel prize in Physics *for the discovery of the exclusion principle.*

1925: *After* studying Pauli's paper, Uhlenbeck and Goudsmit put forward the idea of the spinning electron.

1925 to 1928: In 1925 Heisenberg put forward the 'quantum—theoretical mechanics based exclusively on relationships between quantities observable in principle', which was further developed by Born and Jordan in the same year. The commutation relation was first inroduced by Born and Jordan. Born later wrote 'I shall never forget the thrill I experienced when I succeeded in condensing Heisenberg's ideas on quantum conditions in the mysterious equation $pq - qp = h/2\pi i$'. Schrödinger's papers came in 1926. His three famous papers under the same title 'Quantization as an eigenvalue problem' appeared in quick succession in 1926. In between he had also published a paper with the self-explanatory title 'On the relationship of the Heisenberg-Born-Jordan Quantum Mechanics to mine'. The original papers of Schrödinger, Heisenberg, Born and Jordan are reprinted in Ludwig (1968). In 1926 Born suggested that the square of the wavefunction should be interpreted as the probability density of particles. In 1927 : Heisenberg formulated his famous uncertainty principle* and in the same year Born developed the quantum mechanical theory of scattering of electrons by atoms and Dirac succeeded in developing the quantum theory of radiation which could explain satisfactorily the phenomena of interference as well as the emission and absorption of light by matter**. In 1928 Dirac gave his relativistic equation which led to the prediction of the 'positive electron' which was later called the *positron*. In 1932, Anderson observed such a particle in cosmic radiation where they could be distinguished from electrons by the opposite curvature of their tracks in the presence of a magnetic field.

*Heisenberg's book *The Physical Principles of Quantum Mechanics* is a very entertaining book to read on the uncertainty principle.

**A very nice account of Dirac's quantum theory of radiation has been given in a review paper by Fermi (1932); of course, the classic treatise by Dirac (1958) should be a must for all persons trying to understand quantum mechanics.

The 1932 Nobel prize in Physics went to Heisenberg *for the creation of quantum mechanics*. The 1933 Nobel prize in Physics was shared by Schrödinger and Dirac *for the discovery of new productive forms of atomic theory* and the 1954 Nobel prize in Physics went to Max Born *for his fundamental research in quantum mechanics, especially for his statistical interpretation of the wavefunction.*

1927: Davisson and Germer and independently G. P. Thomson observed electron diffraction patterns produced by metal foils which established the existence of de Broglie waves. The 1937 Nobel prize in Physics was shared by Davisson and Thomson *for their experimental discovery of the diffraction of electrons by crystals.*

1928: Gamow in Germany and Gurney and Condon in USA reported the first major application of quantum mechanics, namely, the barrier leakage interpretation of the natural radioactive decay of some elements emitting alpha particles. The theory could satisfactorily explain the fact that an alpha particle can remain inside a nucleus for about 10^9 years before it comes out. Condon in 1952 wrote: "I think it is fair to say that the barrier-leakage idea was the opening of the modern period of the application of quantum mechanics to nuclear Physics".

1931: In order to explain the continuous beta ray spectrum, Pauli in 1931 suggested the existence of the neutrino.

1934: Fermi developed the famous theory of beta decay.

Although the development of quantum mechanics continues even today, we felt that Fermi's beta decay theory should be an appropriate point to 'sign-off' (keeping in view the scope of the present book). We conclude by mentioning the following incident (quoted from May 1982 issue of *Science Today*):

> After attending a seminar given by one of Oppenheimer's pupils on Fermi's beta ray theory, Fermi remarked to Emilio Segre, 'Emilio, I am getting rusty and old. I cannot follow the highbrow theory developed by Oppenheimer's pupils any more. I went to their seminar and was depressed by my inability to understand them; only the last sentence cheered me up. It was: "And this is Fermi's theory of beta decay".'

WERNER HEISENBERG

The development of quantum mechanics

Nobel Lecture, December 11, 1933

Quantum mechanics, on which I am to speak here, arose, in its formal content, from the endeavour to expand Bohr's principle of correspondence to a complete mathematical scheme by refining his assertions. The physically new viewpoints that distinguish quantum mechanics from classical physics were prepared by the researches of various investigators engaged in analysing the difficulties posed in Bohr's theory of atomic structure and in the radiation theory of light.

In 1900, through studying the law of black-body radiation which he had discovered, Planck had detected in optical phenomena a discontinuous phenomenon totally unknown to classical physics which, a few years later, was most precisely expressed in Einstein's hypothesis of light quanta. The impossibility of harmonizing the Maxwellian theory with the pronouncedly visual concepts expressed in the hypothesis of light quanta subsequently compelled research workers to the conclusion that radiation phenomena can only be understood by largely renouncing their immediate visualization. The fact, already found by Planck and used by Einstein, Debye, and others, that the element of discontinuity detected in radiation phenomena also plays an important part in material processes, was expressed systematically in Bohr's basic postulates of the quantum theory which, together with the Bohr-Sommerfeld quantum conditions of atomic structure, led to a qualitative interpretation of the chemical and optical properties of atoms. The acceptance of these basic postulates of the quantum theory contrasted uncompromisingly with the application of classical mechanics to atomic systems, which, however, at least in its qualitative affirmations, appeared indispensable for understanding the properties of atoms. This circumstance was a fresh argument in support of the assumption that the natural phenomena in which Planck's constant plays an important part can be understood only by largely foregoing a visual description of them. Classical physics seemed the limiting case of visualization of a fundamentally unvisualizable microphysics, the more accurately realizable the more Planck's constant vanishes relative to the parameters of the system. This view of classical mechanics as a limiting case of quantum mechanics also gave rise to Bohr's principle of correspondence which, at least in qualitative terms, transferred a number of conclusions formulated in classical mechanics to quantum mechanics. In connection with the principle of correspondence there was also discussion whether the quantum-mechanical laws could in principle be of a statistical nature; the possibility became particularly apparent in Einstein's derivation of Planck's law of radiation. Finally, the analysis of the relation between radiation theory and atomic theory by Bohr, Kramers and Slater resulted in the following scientific situation:

According to the basic postulates of the quantum theory, an atomic system is capable of assuming discrete, stationary states, and therefore discrete energy values; in terms of the energy of the atom the emission and absorption of light by such a system occurs abruptly, in the form of impulses. On the other hand, the visualizable properties of the emitted radiation are described by a wave field, the frequency of which is associated with the difference in energy between the initial and final states of the atom by the relation

$$E_1 - E_2 = h\nu$$

To each stationary state of an atom corresponds a whole complex of parameters which specify the probability of transition from this state to another. There is no direct relation between the radiation classically emitted by an orbiting electron and those parameters defining the probability of emission; nevertheless Bohr's principle of correspondence enables a specific term of the Fourier expansion of the classical path to be assigned to each transition of the atom, and the probability for the particular transition follows qualitatively similar laws as the intensity of those Fourier components. Although therefore in the researches carried out by Rutherford, Bohr, Sommerfeld and others, the comparison of the atom with a planetary system of electrons leads to a qualitative interpretation of the optical and chemical properties of atoms, nevertheless the fundamental dissimilarity between the atomic spectrum and the classical spectrum of an electron system imposes the need to relinquish the concept of an electron path and to forego a visual description of the atom.

The experiments necessary to define the electron-path concept also furnish an important aid in revising it. The most obvious answer to the question, how the orbit of an electron in its path within the atom could be observed namely, will perhaps be to use a microscope of extreme resolving power. But since the specimen in this microscope would have to be illuminated with light having an extremely short wavelength, the first light quantum from the light source to reach the electron and pass into the observer's eye would eject the electron completely from its path in accordance with the laws of the Compton effect. Consequently only one point of the path would be observable experimentally at any one time.

In this situation, therefore, the obvious policy was to relinquish at first the concept of electron paths altogether, despite its substantiation by Wilson's experiments, and, as it were, to attempt subsequently how much of the electron-path concept can be carried over into quantum mechanics.

In the classical theory the specification of frequency, amplitude, and phase of all the light waves emitted by the atom would be fully equivalent to specifying its electron path. Since from the amplitude and phase of an emitted wave the coefficients of the appropriate term in the Fourier expansion of the electron path can be derived without ambiguity, the complete electron path therefore can be derived from a knowledge of all amplitudes and phases. Similarly, in quantum mechanics, too, the whole complex of amplitudes and phases of the radiation emitted by the atom can be regarded as a complete description of the atomic system, although its interpretation in the sense of an electron path inducing the radiation is impossible. In quantum mechanics, therefore, the place of the electron coordinates is taken by a complex of parameters corresponding to the Fourier coefficients of classical motion along a path. These, however, are no longer classified by the energy of state and the number of the corresponding harmonic vibration, but are in each case associated with two stationary states of the atom, and are a measure for the transition probability of the atom from one stationary state to another. A complex of coefficients of this type is comparable with a matrix such as occurs in linear algebra. In exactly the same way each parameter of classical mechanics, e.g., the momentum or the energy of the electrons, can then be assigned a corresponding matrix in quantum mechanics. To proceed from here beyond a mere description of the empirical state of affairs it was necessary to associate systematically the matrices assigned to the various parameters in the same way as the corresponding parameters in classical mechanics are associated by equations of motions. When, in the interest of achieving the closest possible correspondence between classical and quantum mechanics, the addition and multiplication of Fourier series were tentatively taken as the example for the addition and multiplication of the quantum-theory complexes, the product of two parameters represented by matrices appeared to be most naturally represented by the product matrix in the sense of linear algebra—an assumption already suggested by the formalism of the Kramers-Ladenburg dispersion theory.

It thus seemed consistent simply to adopt in quantum mechanics the equations of motion of classical physics, regarding them as a relation between the matrices representing the classical variables. The Bohr-Sommerfeld quantum conditions could also be re-interpreted in a relation between the matrices, and together with the equations of motion they were sufficient to define all matrices and hence the experimentally observable properties of the atom.

Born, Jordan, and Dirac deserve the credit for expanding the mathematical scheme outlined above into a consistent and practically usable theory. These investigators observed in the first place that the quantum conditions can be written as commutation relations between the matrices representing the momenta and the coordinates of the electrons, to yield the equations (p_r, momentum matrices; q_r, coordinate matrices);

$$p_r q_s - q_s p_r = \frac{h}{2\pi i}\,\delta_{rs} \qquad q_r q_s - q_s q_r = 0 \qquad p_r p_s - p_s p_r = 0$$

$$\delta_{rs} = \begin{cases} 1 \text{ for } r = s \\ 0 \text{ for } r \neq s \end{cases}$$

By means of these commutation relations they were able to detect in quantum mechanics as well the laws which were fundamental to classical mechanics: the invariability in time of energy, momentum, and angular momentum.

The mathematical scheme so derived thus ultimately bears an extensive formal similarity to that of the classical theory, from which it differs outwardly by the commutation relations which, moreover, enabled the equations of motion to be derived from the Hamiltonian function.

In the physical consequences, however, there are very profound differences between quantum mechanics and classical mechanics which impose the need for a thorough discussion of the physical interpretation of quantum mechanics. As hitherto defined, quantum mechanics enables the radiation emitted by the atom, the energy values of the stationary states, and other parameters characteristic for the stationary states to be treated. The theory hence complies with the experimental data contained in atomic spectra. In all those cases, however, where a visual description is required of a transient event, e.g., when interpreting Wilson photographs, the formalism of the theory does not seem to allow an adequate representation of the experimental state of affairs. At this point Schrödinger's wave mechanics, meanwhile developed on the basis of de Broglie's theses, came to the assistance of quantum mechanics.

In the course of the studies which Mr. Schrödinger will report here himself he converted the determination of the energy values of an atom into an eigenvalue problem defined by a boundary-value problem in the coordinate space of the particular atomic system. After Schrödinger had shown the mathematical equivalence of wave mechanics, which he had discovered, with quantum mechanics, the fruitful combination of these two different areas of physical ideas resulted in an extraordinary broadening and enrichment of the formalism of the quantum theory. Firstly, it was only wave mechanics which made possible the mathematical treatment of complex atomic systems, secondly, analysis of the connection between the two theories led to what is known as the transformation theory developed by Dirac and Jordan. As it is impossible within the limits of the present lecture to give a detailed discussion of the mathematical structure of this theory, I should just like to point out its fundamental physical significance. Through the adoption of the physical principles of quantum mechanics into its expanded formalism, the transformation theory made it possible in completely general terms to calculate for atomic systems the probability for the occurrence of a particular, experimentally ascertainable, phenomenon under given experimental conditions. The hypothesis conjectured in the studies on the radiation theory and enunciated in precise terms in Born's collision theory, namely, that the wave function governs the probability for the presence of a corpuscle, appeared to be a special case of a more general pattern of laws and to be a natural consequence of the fundamental assumptions of quantum mechanics. Schrödinger, and in later studies Jordan, Klein, and Wigner as well, had succeeded in developing as far as permitted by the principles of the quantum theory de Broglie's original concept of visualizable matter waves occurring in space and time, a concept formulated even before the development of quantum mechanics. But for that the connection between Schrödinger's concepts and de Broglie's original thesis would certainly have seemed a looser one by this statistical interpretation of wave mechanics and by the greater emphasis on the fact that Schrödinger's theory is concerned with waves in multidimensional space. Before proceeding to discuss the explicit significance of quantum mechanics it is perhaps right for me to deal briefly with this question as to the existence of matter waves in three-dimensional space, since the solution to this problem was only achieved by combining wave and quantum mechanics.

A long time before quantum mechanics was developed Pauli had inferred from the laws in the Periodic System of the elements the well-known principle that a particular quantum state can at all times be occupied by only a single electron. It proved possible to transfer this principle to quantum mechanics on the basis of what at first sight seemed a surprising result: the entire complex of stationary states which an atomic system is capable of adopting breaks down into definite classes such that an atom in a state belonging to one class can never change into a state belonging to another class under the action of whatever perturbations. As finally clarified beyond question by the studies of Wigner and Hund, such a class of states is characterized by a definite symmetry characteristic of the Schrödinger eigenfunction with respect to the transposition of the coordinates of two electrons. Owing to the fundamental identity of electrons, any external perturbation of the atom remainsunc hanged when two electrons are exchanged and hence causes no transitions between states of various classes. The Pauli principle and the Fermi-Dirac statistics derived from it are equivalent with the assumption that only that class of stationary states is achieved in nature in which the eigenfunction changes its sign when two electrons are exchanged. According to Dirac, selecting the symmetrical system of terms would lead not to the Pauli principle, but to Bose-Einstein electron statistics.

Between the classes of stationary states belonging to the Pauli principle or to Bose-Einstein statistics, and de Broglie's concept of matter waves there is a peculiar relation. A spatial wave phenomenon can be treated according to the principles of the quantum theory by analysing it using the Fourier theorem and then applying to the individual Fourier component of the wave motion, as a system having one degree of freedom, the normal laws of quantum mechanics. Applying this procedure for treating wave phenomena by the quantum theory, a procedure that has also proved fruitful in Dirac's studies of the theory of radiation, to de Broglie's matter waves, exactly the same results are obtained as in treating a whole complex of material particles according to quantum mechanics and selecting the symmetrical system of terms. Jordan and Klein hold that the two methods are mathematically-equivalent even if allowance is also made for the interaction of the electrons, i.e., if the field energy originating from the continuous spaco charge is included in the calculation in de Broglie's wave theory. Schrödinger's considerations of the energy-momentum tensor assigned to the matter waves can then also be adopted in this theory as consistent components of the formalism. The studies of Jordan and Wigner show that modifying the commutation relations underlying this quantum theory of waves results in a formalism equivalent to that of quantum mechanics based on the assumption of Pauli's exclusion principle.

These studies have established that the comparison of an atom with a planetary system composed of nucleus and electrons is not the only visual picture of how we can imagine the atom. On the contrary, it is apparently no less correct to compare the atom with a charge cloud and use the correspondence to the formalism of the quantum theory borne by this concept to derive qualitative conclusions about the behaviour of the atom. However, it is the concern of wave mechanics to follow these consequences.

Reverting therefore to the formalism of quantum mechanics; its application to physical problems is justified partly by the original basic assumptions of the theory, partly by its expansion in the transformation theory on the basis of wave mechanics, and the question is now to expose the explicit significance of the theory by comparing it with classical physics.

In classical physics the aim of research was to investigate objective process occurring in space and time, and to discover the laws governing their progress from the initial conditions. In classical physics a problem was considered solved when a particular phenomenon had been proved to occur objectively in space and time, and it had been shown to obey the general rules of classical physics as formulated by differential equations. The manner in which the knowledge of each process had been acquired, what observations may possibly have led to its experimental determination, was completely immaterial, and it was also immaterial for the consequences of the classical theory, which possible observations were to verify the predictions of the theory. In the quantum theory, however, the situation is completely different. The very fact that the formalism of quantum mechanics cannot be interpreted as visual-description of a phenomenon occurring in space and time shows that quantum mechanics is in no way concerned with the objective determination of space-time phenomena. On the contrary, the formalism of quantum mechanics should be used in such a way that the probability for the outcome of a further experiment may be concluded from the determination of an experimental situation in an atomic system, providing that the system is subject to no perturbations other than those necessitated by performing the two experiments. The fact that the only definite known result to be ascertained after the fullest possible experimental investigation of the system is the probability for a certain outcome of a second experiment shows, however, that each observation must entail a discontinuous change in the formalism describing the atomic process and therefore also a discontinuous change in the physical phenomenon itself. Whereas in the classical theory the kind of observation has no bearing on the event, in the quantum theory the disturbance associated with each observation of the atomic phenomenon has a decisive role. Since, furthermore, the result of an observation as a rule leads only to assertions about the probability of certain results of subsequent observations, the fundamentally unverifiable part of each perturbation must, as shown by Bohr, be decisive for the non-contradictory operation of quantum mechanics. This difference between classical and atomic physics is understandable, of course, since for heavy bodies such as the planets moving around the sun the pressure of the sunlight which is reflected at their surface and which is necessary for them to be observed is negligible: for the smallest building units of matter, however, owing to their low mass, every observation has a decisive effect on their physical behaviour.

The perturbation of the system to be observed caused by the observation is also an important factor in determining the limits within which a visual description of atomic phenomena is possible. If there were experiments which permitted accurate measurement of all the characteristics of an atomic system necessary to calculate classical motion, and which, for example, supplied accurate values for the location and velocity of each electron in the system at a particular time, the result of these experiments could not be utilized at all in the formalism, but rather it would directly contradict the formalism. Again, therefore, it is clearly that fundamentally unverifiable part of the perturbation of the system caused by the measurement itself which hampers accurate ascertainment of the classical characteristics and thus permits quantum mechanics to be applied. Closer examination of the formalism shows that between the accuracy with which the location of a particle can be ascertained and the accuracy with which its momentum can simultaneously be known, there is a relation according to which the product of the probable errors in the measurement of the location and momentum is invariably at least as large as Planck's constant divided by 4π. In a very general form, therefore, we should have

$$\Delta p \, \Delta q \geqslant \frac{h}{4\pi}$$

where p and q are canonically conjugated variables. These uncertainty relations for the results of the measurement of classical variables form the necessary conditions for enabling the result of a measurement to be expressed in the formalism of the quantum theory. Bohr has shown in a series of examples how the perturbation necessarily, associated with each observation indeed ensures that one cannot go below the limit set by the uncertainty relations. He contends that in the final analysis an uncertainty introduced by the concept of measurement itself is responsible for part of that perturbation remaining fundamentally unknown. The experimental determination of whatever space-time events invariably necessitates a fixed frame—say the system of coordinates in which the observer is at rest—to which all measurements are referred. The assumption that this frame is ⟨⟨fixed⟩⟩ implies neglecting its momentum from the outset, since ⟨⟨fixed⟩⟩ implies nothing other, of course, than that any transfer of momentum to it will evoke no perceptible effect. The fundamentally necessary uncertainty at this point is then transmitted via the measuring apparatus into the atomic event.

Since in connection with this situation it is tempting to consider the possibility of eliminating all uncertainties by amalgamating the object, the measuring apparatuses, and the observer into one quantum-mechanical system, it is important to emphasize that the act of measurement is necessarily visualizable, since, of course, physics is ultimately only concerned with the systematic description of space-time processes. The behaviour of the observer as well as his measuring apparatus must therefore be discussed according to the laws of classical physics, as otherwise there is no further physical problem whatsoever. Within the measuring apparatus, as emphasized by Bohr, all events in the sense of the classical theory will therefore be regarded as determined, this also being a necessary condition before one can, from a result of measurements, unequivocally conclude what has happened. In quantum theory, too, the scheme of classical physics which objectifies the results of observation by assuming in space and time processes obeying laws is thus carried through up to the point where the fundamental limits are imposed by the unvisualizable character of the atomic events symbolized by Planck's constant. A visual description for the atomic events is possible only within certain limits of accuracy—but within these limits the laws of classical physics also still apply. Owing to these limits of accuracy as defined by the uncertainty relations, moreover, a visual picture of the atom free from ambiguity has not been determined. On the contrary the corpuscular and the wave concepts are equally serviceable as a basis for visual interpretation.

The laws of quantum mechanics are basically statistical. Although the parameters of an atomic system are determined in their entirety by an experiment, the result of a future observation of the system is not generally accurately predictable. But at any later point of time there are observations which yield accurately predictable results. For the other observations only the probability for a particular outcome of the experiment can be given. The degree of certainty which still attaches to the laws of quantum mechanics is, for example, responsible for the fact that the principles of conservation for energy and momentum still hold as strictly as ever. They can be checked with any desired accuracy and will then be valid according to the accuracy with which they are checked. The statistical character of the laws of quantum mechanics, however, becomes apparent in that an accurate study of the energetic conditions renders it impossible to pursue at the same time a particular event in space and time.

For the clearest analysis of the conceptual principles of quantum mechanics we are indebted to Bohr who, in particular, applied the concept of complementarity to interpret the validity of the quantum mechanical laws. The uncertainty relations alone afford an instance of how in quantum mechanics the exact knowledge of one variable can exclude the exact knowledge of another. This complementary relationship between different aspects of one and the same physical process is indeed characteristic for the whole structure of quantum mechanics. I had just mentioned that, for example, the determination of energetic relations excludes the detailed description of space-time processes. Similarly, the study of the chemical properties of a molecule is complementary to the study of the motions of the individual electrons in the molecule, or the observation of interference phenomena complementary to the observation of individual light quanta. Finally, the areas of validity of classical and quantum mechanics can be marked off one from the other as follows: Classical physics represents that striving to learn about Nature in which essentially we seek to draw conclusions about objective processes from observations and so ignore the consideration of the influences which every observation has on the object to be observed; classical physics, therefore, has its limits at the point from which the influence of the observation on the event can no longer be ignored. Conversely, quantum mechanics makes possible the treatment of atomic processes by partially foregoing their space-time description and objectification.

So as not to dwell on assertions in excessively abstract terms about the interpretation of quantum mechanics, I would like briefly to explain with a well-known example how far it is possible through the atomic theory to achieve an understanding of the visual processes with which we are concerned in daily life. The interest of research workers has frequently been focused on the phenomenon of regularly shaped crystals suddenly forming from a liquid, e.g., a supersatured salt solution. According to the atomic theory the forming force in this process is to a certain extent the symmetry characteristic of the solution to Schrödinger's wave equation, and to that extent crystallization is explained by the atomic theory. Nevertheless this process retains a statistical and—one might almost say—historical element which cannot be further reduced: even when the state of the liquid is completely known before crystallization, the shape of the crystal is not determined by the laws of quantum mechanics. The formation of regular shapes is just far more probable than that of a shapeless lump. But the ultimate shape owes its genesis partly to an element of chance which in principle cannot be analysed further.

Before closing this report on quantum mechanics, I may perhaps be allowed to discuss very briefly the hopes that may be attached to the further development of this branch of research. It would be superfluous to mention that the development must be continued, based equally on the studies of de Broglie, Schrödinger, Born, Jordan and Dirac. Here the attention of the research workers is primarily directed to the problem of reconciling the claims of the special relativity theory with those of the quantum theory. The extraordinary advances made in this field by Dirac about which Mr. Dirac will speak here, meanwhile leave open the question whether it will be possible to satisfy the claims of the two theories without at the same time determining the Sommerfeld fine-structure constant. The attempts made hitherto to achieve a relativistic formulation of the quantum theory are all based on visual concepts so close to those of classical physics that it seems impossible to determine the fine-structure constant within this system of concepts. The expansion of the conceptual system under discussion here should, furthermore, be closely associated with the further development of the quantum theory of wave fields, and it appears to me as if this formalism, notwithstanding its thorough study by a number of workers (Dirac, Pauli, Jordan, Klein, Wigner, Fermi) has still not been completely exhausted. Important pointers for the further development of quantum mechanics also emerge from the experiments involving the structure of the atomic nuclei. From their analysis by means of the Gamow theory, it would appear that between the elementary particles of the atomic nucleus forces are at work which differ somewhat in type from the forces determining the structure of the atomic shell; Stern's experiments seem, furthermore, to indicate that the behaviour of the heavy elementary particles cannot be represented by the formalism of Dirac's theory of the electron Future research will thus have to be prepared for surprises which may otherwise come both from the field of experience of nuclear physics as well as from that of cosmic radiation. But however the development proceeds in detail, the path so far traced by the quantum theory indicates that an understanding of those still unclarified features of atomic physics can only be acquired by foregoing visualization and objectification to an extent greater than that customary hitherto. We have probably no reason to regret this, because the thought of the great epistemological difficulties with which the visual atom concept of earlier physics had to contend gives us the hope that the abstracter atomic physics developing at present will one day fit more harmoniously into the great edifice of Science.

ERWIN SCHRÖDINGER

The fundamental idea of wave mechanics

Nobel Lecture, December 12, 1933

On passing through an optical instrument, such as a telescope or a camera lens, a ray of light is subjected to a change in direction at each refracting or reflecting surface. The path of the rays can be constructed if we know the two simple laws which govern the changes in direction: the law of refraction which was discovered by Snellius a few hundred years ago, and the law of reflection with which Archimedes was familiar more than 2,000 years ago. As a simple example, Fig. 1 shows a ray A-B which is subjected to refraction at each of the four boundary surfaces of two lenses in accordance with the law of Snellius.

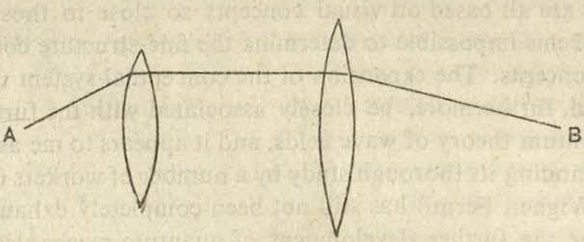

Fig. 1.

Fermat defined the total path of a ray of light from a much more general point of view. In different media, light propagates with different velocities, and the radiation path gives the appearance as if the light must arrive at its destination *as quickly as possible.* (Incidentally, it is permissible here to consider *any two* points along the ray as the starting- and end-points.) The least deviation from the path actually taken would mean a delay. This is the famous Fermat *principle of the shortest light time*, which in a marvellous manner determines the entire fate of a ray of light by a single statement and also includes the more general case, when the nature of the medium varies not suddenly at individual surface, but gradually from place to place. The atmosphere of the earth provides an example. The more deeply a ray of light penetrates into it from outside, the more slowly it progresses in an increasingly denser air. Although the differences in the speed of propagation are infinitesimal, Fermat's principle in the circumstances demands that the light ray should curve earthward (see Fig. 2), so that it remains a little longer in the higher ⟨⟨faster⟩⟩ layers and reaches its destination more quickly than by the shorter straight path (broken line in the figure; disregard the square, WWW^1W^1 for the time being). I think, hardly any of you will have failed to observe that the sun when it is deep on the horizon appears to be not circular but flattened: its vertical diameter looks to be shortened. This is a result of the curvature of the rays.

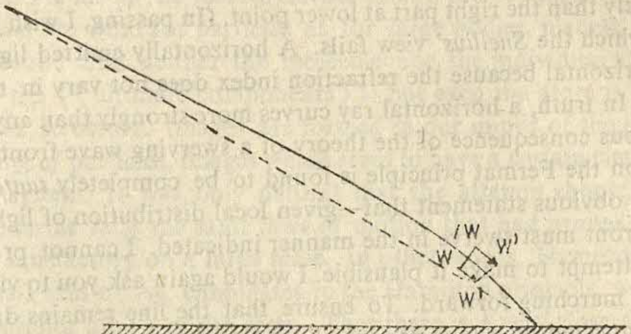

Fig. 2.

According to the wave theory of light, the light rays, strictly speaking, have only fictitious significance. They are not the physical paths of some particles of light, but are a mathematical device, the so-called orthogonal trajectories of wave surfaces, imaginary guidelines as it were, which point in the direction normal to the wave surface in which the latter advances (cf. Fig. 3 which shows the simplest case of concentric spherical wave surfaces and accordingly rectilinear rays, whereas Fig. 4 illustrates the case of curved rays). It is surprising that a general principle as important as Fermat's relates directly to these mathematical guidelines, and not to the wave surfaces, and one might be inclined for this reason to consider it a mere mathematical curiosity. Far from it, it becomes properly understandable only from the point of view of wave theory and ceases to be a divine miracle. From the wave point of view, the so-called *curvature* of the light ray is far more readily understandable as a *swerving* of the wave surface, which must obviously occur when neighbouring parts of a wave surface advance at different speeds; in exactly the same manner as a company of soldiers marching forward will carry out the order ⟨⟨right incline⟩⟩ by the men taking steps of varying lengths, the right-wing man the smallest, and the left-wing man

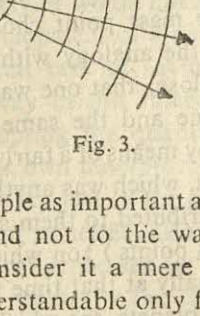

Fig. 3.

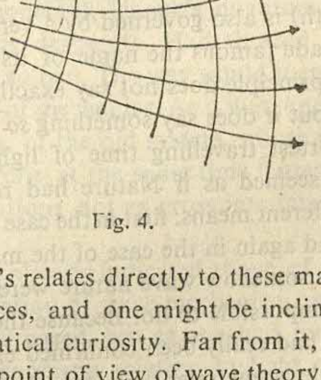

Fig. 4.

the longest. In atmospheric refraction of radiation for example (Fig. 2) the section of wave surface WW must necessarily swerve to the right towards W^1W^1 because its left half is located in slightly higher, thinner air and thus advances more rapidly than the right part at lower point. (In passing, I wish to refer to one point at which the *Snellius*' view fails. A horizontally emitted light ray should remain horizontal because the refraction index does not vary in the horizontal direction. In truth, a horizontal ray curves more strongly than any other, which is an obvious consequence of the theory of a swerving wave front.) On detailed examination the Fermat principle is found to be completely *tantamount* to the trivial and obvious statement that—given local distribution of light velocities—the wave front must swerve in the manner indicated. I cannot prove this here, but shall attempt to make it plausible. I would again ask you to visualize a rank of soldiers marching forward. To ensure that the line remains dressed, let the men be connected by a long rod which each holds firmly in his hand. No orders as to direction are given: the only order is: let each man march or run as fast as he can. If the nature of the ground varies slowly from place to place, it will be now the right wing, now the left that advances more quickly, and changes in direction will occur spontaneously. After some time has elapsed, it will be seen that the entire path travelled is not rectilinear, but somehow curved. That this curved path is exactly that by which the destination attained at any moment could be attained *most rapidly* according to the nature of the terrain, is at least quite plausible, since each of the men did his best. It will also be seen that the swerving also occurs invariably in the direction in which the terrain is worse so that it will come to look in the end as if the men had ⟨⟨intentionally⟩⟩ bypassed a place where they would advance slowly.

The Fermat principle thus appears to be the *trivial quintessence* of the wave theory. It was therefore a memorable occasion when Hamilton made the discovery that the true movement of mass points in a field of forces (e.g., of a planet on its orbit around the sun or of a stone thrown in the gravitational field of the earth) is also governed by a very similar general principle, which carries and has made famous the name of its discoverer since then. Admittedly, the Hamilton principle does not say exactly that the mass point chooses the quickest way, but it does say something *so* similar—the analogy with the principle of the shortest travelling time of light is *so* close, that one was faced with a puzzle. It seemed as if Nature had realized one and the same law twice by entirely different means: first in the case of light, by means of a fairly obvious play of rays; and again in the case of the mass points, which was anything but obvious, unless somehow wave nature were to be attributed to them also. And this, it seemed impossible to do. Because the ⟨⟨mass points⟩⟩ on which the laws of mechanics had really been confirmed experimentally at that time were only the large, visible, sometimes *very* large bodies, the planets, for which a thing like ⟨⟨wave nature⟩⟩ appeared to be out of the question.

The smallest, elementary components of matter which we today, much more specifically, call ⟨⟨mass points⟩⟩, were purely hypothetical at the time. It was only after the discovery of radioactivity that constant refinements of methods of measurement permitted the properties of these particles to be studied in detail, and now permit the paths of such particles to be photographed and to be measured very exactly (stereophotogrammetrically) by the brilliant method of C.T.R. Wilson. As far as the measurements extend they confirm that the same mechanical laws are valid for particles as for large bodies, planets, etc. However, it was found that neither the molecule nor the individual atom can be considered as the ⟨⟨ultimate components⟩⟩: but even the atom is a system of highly complex structure. Images are formed in our minds of the structure of atoms *consisting of* particles, images which seem to have a certain similarity with the planetary system. It was only natural that the attempt should at first be made to consider as valid the same laws of motion that had proved themselves so amazingly satisfactory on a large scale. In other words, Hamilton's mechanics, which, as I said above, culminates in the Hamilton principle, were applied also to the ⟨⟨inner life⟩⟩ of the atom. That there is a very close analogy between Hamilton's principle and Fermat's optical principle had meanwhile become all but forgotten. If it was remembered, it was considered to be nothing more than a curious trait of the mathematical theory.

Now, it is very difficult, without further going into details, to convey a proper conception of the success or failure of these classical-mechanical images of the atom. On the one hand Hamilton's principle in particular proved to be the most faithful and reliable guide, which was simply indispensable; on the other hand one had to suffer, to do justice to the facts, the rough interference of entirely new incomprehensible postulates, of the so-called quantum conditions and quantum postulates. Strident-disharmony in the symphony of classical mechanics—yet strangely familiar—played as it were on the same instrument. In mathematical terms we can formulate this as follows: whereas the Hamilton principle merely postulates that a given integral must be a minimum, without the numerical value of the minimum being established by this postulate, it is now demanded that the numerical value of the minimum should be restricted to integral multiples of a universal natural constant, Planck's quantum of action. This incidentally. The situation was fairly desperate. Had the old mechanics failed completely, it would not have been so bad. The way would then have been free to the development of a new system of mechanics. As it was, one was faced with the difficult task of saving the *soul* of the old system, whose inspiration clearly held sway in this microcosm, while at the same time flattering it as it were into accepting the quantum conditions not as gross interference but as issuing from its own innermost essence.

The way out lay just in the possibility, already indicated above, of attributing to the Hamilton principle, also, the operation of wave mechanism on which the point-mechanical processes are essentially based, just as one had long become accustomed to doing in the case of phenomena relating to light and of the Fermat principle which governs them. Admittedly, the individual path of a mass point loses its proper physical significance and becomes as fictitious as the individual isolated ray of light. The essence of the theory, the minimum principle, however, remains not only intact, but reveals its true and simple meaning only under the wave-like aspect, as already explained. Strictly speaking, the new theory is in fact *not new*, it is a completely organic development, one might almost be tempted to say a more elaborate exposition, of the old theory.

How was it then that this new more ⟨⟨elaborate⟩⟩ exposition led to notably different result; what enabled it, when applied to the atom, to obviate difficulties which the old theory could not solve? What enabled it to render gross interference acceptable or even to make it its own?

Again, these matters can best be illustrated by analogy with optics. Quite properly, indeed I previously called the Fermat principle the quintessence of the wave theory of light: nevertheless, it cannot render dispensible a more exact study of the wave process itself. The so-called refraction and interference phenomena of light can only be understood if we trace the wave process in detail because what matters is not only the eventual destination of the wave, but also whether at a given moment it arrives there with a wave peak or a wave trough. In the older, coarser experimental arrangements, these phenomena occurred as small details only and escaped observation. Once they were noticed and were interpreted correctly, by means of waves, it was easy to devise experiments in which the wave nature of light finds expression not only in small details, but on a very large scale in the entire character of the phenomena.

Allow me to illustrate this by two examples, first, the example of an optical instrument, such as telescope, microscope, etc. The object is to obtain a sharp image, i.e., it is desired that all rays issuing from a point should be reunited in a point, the so-called focus (cf. Fig. 5a). It was at first believed that it was only geometrical-optical difficulties which prevented this: they are indeed considerable.

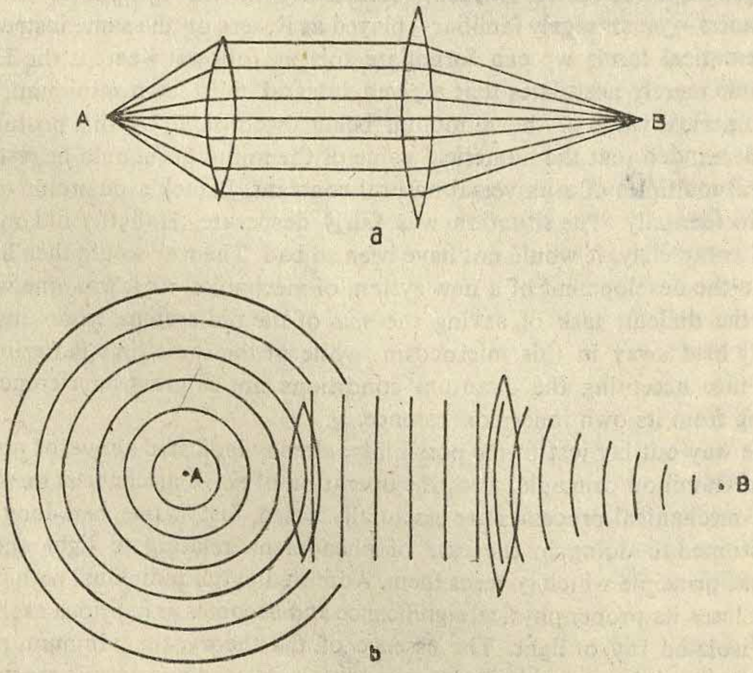

Fig. 5.

Later it was found that even in the best designed instruments focussing of the rays was considerably inferior than would be expected if each ray exactly obeyed the Fermat principle independently of the neighbouring rays. The light which issues from a point and is received by the instrument is reunited behind the instrument not in a single point any more, but is distributed over a small circular area, a so-called diffraction disc, which, otherwise, is in most cases a circle only because the apertures and lens contours and generally circular. For, the cause of the phenomenon which we call *diffraction* is that not all the spherical waves issuing from the object point can be accommodated by the instrument. The lens edges and any apertures merely cut a part of the wave surfaces (cf. Fig. 5b) and—if you will permit me to use a more suggestive expression—the injured margins resist rigid unification in a point and produce the somewhat blurred or vague image. The degree of blurring is closely associated with the *wavelength* of the light and is completely inevitable because of this deep-seated theoretical relationship. Hardly noticed at first, it governs and restricts the performance of the modern microscope which has mastered all other errors of reproduction. The images obtained of structures not much coarser or even still finer than the wavelengths of light are only remotely or not at all similar to the original.

A second, even simple example, is the shadow of an opaque object cast on a screen by a small point light source. In order to construct the shape of the shadow, each light ray must be traced and it must be established whether or not the opaque object prevents it from reaching the screen. The *margin* of the shadow is formed by those light rays which only just brush past the edge of the body. Experience has shown that the shadow margin is not absolutely sharp even with a point-shaped light source and a sharply defined shadow-casting object. The reason for this is the same as in the first example. The wave front is as it were bisected by the body (cf. Fig. 6) and the traces of this injury result in blurring of the margin of the shadow which would be incomprehensible if the individual light rays were independent entities advancing independently of one another without reference to their neighbours.

This phenomenon—which is also called diffraction—is not as a rule very noticeable with large bodies. But if the shadow-casting body is very small at least in one dimension, diffraction finds expression firstly in that no proper shadow is formed at all, and secondly—much more strikingly—in that the small body itself becomes as it were its own source of light and radiates light in all directions (preferentially to be sure, at small angles relative to the incident light). All of you are undoubtedly familiar with the so-called ⟨⟨motes of dust⟩⟩ in a light beam falling into a dark room. Fine blades of grass and spiders webs on the crest of a hill with the sun behind it, or the errant locks of hair of a man standing with the sun behind often light up mysteriously by diffracted light, and the visibility of smoke and mist is based on it. It comes not really from the body itself, but from its immediate surroundings, an area in which it causes considerable interference with the incident wave fronts. It is interesting and important for what follows, to observe that the area of interference always and in every direction has at least the extent of one or a few wave lengths, no matter how small the disturbing particle may be. Once again, therefore, we observe a close

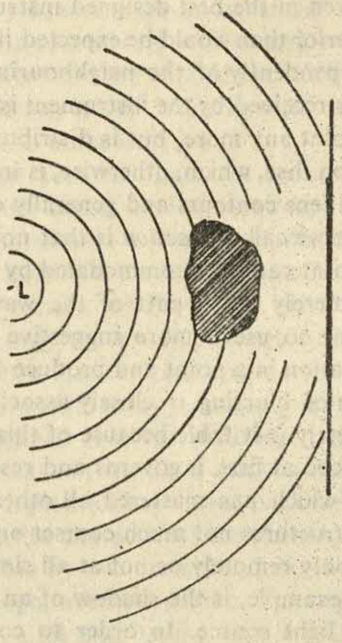

Fig. 6

relationship between the phenomenon of diffraction and wavelength. This is perhaps best illustrated by reference to another wave process, i.e., sound. Because of the much greater wavelength, which is of the order of centimeters and meters, shadow formation recedes in the case of sound, and diffraction plays a major, and practically important, part: we can easily *hear* a man calling from behind a high wall or around the corner of a solid house, even if we cannot *see* him.

Let us return from optics to mechanics and explore the analogy to its fullest extent. In optics the *old* system of mechanics corresponds to intellectually operating with isolated mutually independent light rays. The new undulatory mechanics corresponds to the wave theory of light. What is gained by changing from the old view to the new is that the diffraction phenomena can be accommodated or, better expressed, what is gained is something that is strictly analogous to the diffraction phenomena of light and which on the whole must be very unimportant, otherwise the old view of mechanics would not have given full satisfaction so long. It is, however, easy to surmise that the neglected phonomenon may in some circumstances make itself very much felt, will entirely dominate the mechanical process and will face the old system with insoluble riddles, if *the entire mechanical system is comparable in extent with the wavelengths of the* ⟨⟨*waves of matter*⟩⟩ which play the same part in mechanical processes as that played by the light waves in optical processes.

This is the reason why in these minute systems, the atoms, the old view was bound to fail, which though remaining intact as a close approximation for gross mechanical processes, but is no longer adequate for the delicate interplay in areas of the order of magnitude of one or a few wavelengths. It was astounding to observe the manner in which all those strange additional requirements developed spontaneously from the new undulatory view, whereas they had to be forced upon the old view to adapt them to the inner life of the atom and to provide some explanation of the observed facts.

Thus, the salient point of the whole matter is that the diameters of the atoms and the wavelength of the hypothetical material waves are of approximately the same order of magnitude. And now you are bound to ask whether it must be considered mere chance that in our continued analysis of the structure of matter we should come upon the order of magnitude of the wavelength at this of all points, or whether this is to some extent comprehensible. Further, you may ask, how we know that this is so, since the material waves are an entirely new requirement of this theory, unknown anywhere else. Or is it simply that this is an *assumption* which had to be made?

The agreement between the orders of magnitude is no mere chance, nor is any special assumption about it necessary: it follows automatically from the theory in the following remarkable manner. That the heavy *nucleus* of the atom is very much smaller than the atom and may therefore be considered as a point centre of attraction in the argument which follows may be considered as experimentally established by the experiments on the scattering of alpha rays done by Rutherford and Chadwick. Instead of the *electrons* we introduce hypothetical waves, whose wavelengths are left entirely open, because we know nothing about them yet. This leaves a letter, say *a*, indicating a still unknown figure, in our calculation. We are, however, used to this in such calculations and it does not prevent us from calculating that the nucleus of the atom must produce a kind of diffraction phenomenon in these waves, similarly as a minute dust particle does in light waves. Analogously, it follows that there is a close relationship between the extent of the area of interference with which the nucleus surrounds itself and the wavelength, and that the two are of the same order of magnitude. What this is, we have had to leave open; but the most important step now follows: *we identify the area of interference, the diffraction halo, with the atom; we assert that the atom in reality is merely the diffraction phenomenon of an electron wave captured as it were by the nucleus of the atom.* It is no longer a matter of chance that the size of the atom and the wavelength are of the same order of magnitude: it is a matter of course. We know the numerical value of neither, because we still have in our calculation the *one* unknown constant, which we called *a*. There are two possible ways of determining it, which provide a mutual check on one another. First, we can so select it that the manifestations of life of the atom, above all the spectrum lines emitted, come out correctly quantitatively; these can after all be measured very accurately. Secondly, we can select *a* in a manner such that the diffraction halo acquires the size required for the atom. These two determinations of *a* (of which the second is admittedly far more imprecise because ⟨⟨size of the atom⟩⟩ is no clearly defined term) *are in complete agreement with one another*. Thirdly, and lastly, we can remark that the constant remaining unknown, physically speaking, does not in fact have the dimension of a length, but of an action, i.e., energy × time. It is then an obvious step to substitute for it the numerical value of Planck's universal quantum of action, which is accurately known from the laws of heat radiation. It will be seen that *we return*, with the full, now considerable accuracy, *to the first* (most accurate) *determination*.

Quantitatively speaking, the theory therefore manages with a minimum of new assumptions. It contains a single available constant, to which a numerical value familiar from the older quantum theory must be given, first to attribute to the diffraction halos the right size so that they can be reasonably identified with the atoms, and secondly, to evaluate quantitatively and correctly all the manifestations of life of the atom, the light radiated by it, the ionization energy, etc.

I have tried to place before you the fundamental idea of the wave theory of matter in the simplest possible form. I must admit now that in my desire not to tangle the ideas from the very beginning, I have painted the lily. Not as regards the high degree to which all sufficiently, carefully drawn conclusions are confirmed by experience, but with regard to the conceptual ease and simplicity with which the conclusions are reached. I am not speaking here of the mathematical difficulties, which always turn out to be trivial in the end, but of the conceptual difficulties. It is, of course, easy to say that we turn from the concept of a *curved path* to a system of wave surfaces normal to it. The wave surfaces, however, even if we consider only small parts of them (see Fig. 7) include at least a narrow *bundle* of possible curved paths, to all of which they stand in the same relationship. According to the old view, but not according to the new, one of them in each concrete individual case is distinguished from all the others which are ⟨⟨only possible⟩⟩, as that ⟨⟨really travelled⟩⟩. We are facedh ere with the full force of the logical opposition between an

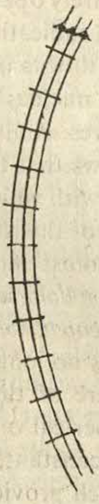

Fig. 7

either – or (point mechanics)

and a

both – and (wave mechanics)

This would not matter much, if the old system were to be dropped entirely and to be *replaced* by the new. Unfortunately, this is not the case. From the point of view of wave mechanics, the infinite array of possible point paths would be merely fictitious, none of them would have the prerogative over the others of being that really travelled in an individual case. I have, however, already mentioned that we have yet really observed such individual particle paths in some cases. The wave theory can represent this, either not at all or only very imperfectly. We find it confoundedly difficult to interpret the traces we *see* as nothing more than narrow bundles of equally possible paths between which the wave surfaces establish cross-connections. Yet, these cross-connections are necessary for an understanding of the diffraction and interference phenomena which can be demonstrated for the same particle with the same plausibility—and that on a large scale, not just as a consequence of the theoretical ideas about the interior of the atom which we mentioned earlier. Conditions are admittedly such that we can always manage to make do in each concrete individual case without the two different aspects leading to different expectations as to the result of certain experiments. We cannot, however, manage to make do with such old, familiar, and seemingly indispensible terms as ⟨⟨real⟩⟩ or ⟨⟨only possible⟩⟩; we are never in a position to say what really *is* or what really *happens*, but we can only say what will be *observed* in an any concrete individual case. Will we have to be permanently satisfied with this . . . ? On principle, yes. On principle, there is nothing new in the postulate that in the end exact science should aim at nothing more than the description of what can really be observed. The question is only whether from now on we shall have to refrain from tying description to a clear hypothesis about the real nature of the world. There are many who wish to pronounce such abdication even today. But I believe that this means making things a little too easy for oneself.

I would define the present state of our knowledge as follows. The ray or the particle path corresponds to a *longitudinal* relationship of the propagation process (i.e., *in the direction* of propagation), the wave surface on the other hand to a *transversal* relationship (i.e., *normal* to it). *Both* relationships are without doubt real: one is proved by photographed particle paths, the other by interference experiments. To combine both in a uniform system has proved impossible so far. Only in extreme cases does either the transversal, shell-shaped or the radial, longitudinal relationship predominate to such an extent that we *think* we can make do with the wave theory alone or with the particle theory alone.

PAUL A. M. DIRAC

Theory of electrons and positrons

Nobel Lecture, December 12, 1933

Matter has been found by experimental physicists to be made up of small particles of various kinds, the particles of each kind being all exactly alike. Some of these kinds have definitely been shown to be composite, that is, to be composed of other particles of a simpler nature. But there are other kinds which have not been shown to be composite and which one expects will never be shown to be composite, so that one considers them as elementary and fundamental.

From general philosophical grounds one would at first sight like to have as few kinds of elementary particles as possible, say only one kind, or at most two, and to have all matter built up of these elementary kinds. It appears from the experimental results, though, that there must be more than this. In fact the number of kinds of elementary particle has shown a rather alarming tendency to increase during recent years.

The situation is perhaps not so bad, though, because on closer investigation it appears that the distinction between elementary and composite particles cannot be made rigorous. To get an interpretation of some modern experimental results one must suppose that particles can be created and annihilated. Thus if a particle is observed to come out from another particle, one can no longer be sure that the latter is composite. The former may have been created. The distinction between elementary particles and composite particles now becomes a matter of convenience. This reason alone is sufficient to compel one to give up the attractive philosophical idea that all matter is made up of one kind, or perhaps two kinds of bricks.

I should like here to discuss the simpler kinds of particles and to consider *what can be inferred about them from purely theoretical arguments.* The simpler kinds of particle are:

(i) the photons or light-quanta, of which light is composed;
(ii) the electrons, and the recently discovered positrons (which appear to be a sort of mirror image of the electrons, differing from them only in the sign of their electric charge);
(iii) the heavier particles—protons and neutrons.

Of these, I shall deal almost entirely with the electrons and the positrons—not because they are the most interesting ones, but because in their case the theory has been developed further. There is, in fact, hardly anything that can be inferred theoretically about the properties of the others. The photons, on the one hand, are so simple that they can easily be fitted into any theoretical scheme and

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the theory therefore does not put any restrictions on their properties. The protons and neutrons, on the other hand, seem to be too complicated and no reliable basis for a theory of them has yet been discovered.

The question that we must first consider is how theory can give any information at all about the properties of elementary particles. There exists at the present time a general quantum mechanics which can be used to describe the motion of any kind of particle, no matter what its properties are. The general quantum mechanics, however, is valid only when the particles have small velocities and fails for velocities comparable with the velocity of light, when effects of relativity come in. There exists no relativistic quantum mechanics (that is, one valid for large velocities) which can be applied to particles with arbitrary properties. Thus when one subjects quantum mechanics to relativistic requirements, one imposes restrictions on the properties of the particle. In this way one can deduce information about the particles from purely theoretical considerations, based on general physical principles.

This procedure is successful in the case of electrons and positrons. It is to be hoped that in the future some such procedure will be found for the case of the other particles. I should like here to outline the method for electrons and positrons, showing how one can deduce the spin properties of the electron, and then how one can infer the existence of positrons with similar spin properties and with the possibility of being annihilated in collisions with electrons.

We begin with the equation connecting the kinetic energy W and momentum p_r, $(r = 1, 2, 3)$, of a particle in relativistic classical mechanics

$$\frac{W^2}{c^2} - p_r^2 - m^2c^2 = 0 \tag{1}$$

From this we can get a wave equation of quantum mechanics, by letting the left-hand side operate on the wave function Ψ and understanding W and p_r to be the operators $ih\partial/\partial t$ and $-ih\partial/\partial x_r$. With this understanding, the wave equation reads

$$\left[\frac{W^2}{c^2} - p_r^2 - m^2c^2\right]\Psi = 0 \tag{2}$$

Now it is a general requirement of quantum mechanics that its wave equations shall be linear in the operator W or $\partial/\partial t$, so this equation will not do. We must replace it by some equation linear in W, and in order that this equation may have relativistic invariance it must also be linear in the p's.

We are thus led to consider an equation of the type

$$\left[\frac{W}{c} - \alpha_r p_r - \alpha_0 mc\right]\Psi = 0 \tag{3}$$

This involves four new variables α_r and α_0, which are operators that can operate on Ψ. We assume they satisfy the following conditions.

$$\alpha_\mu^2 = 1 \qquad \alpha_\mu\alpha_\nu + \alpha_\nu\alpha_\mu = 0$$

for

$$\mu \neq \nu \qquad \text{and} \qquad \mu, \nu = 0, 1, 2, 3$$

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and also the α's commute with the p's and W. These special properties for the α's make Eq. (3) to a certain extent equivalent to Eq. (2), since if we then multiply (3) on the left-hand side by $W/c + \alpha_r p_r + \alpha_0 mc$ we get exactly (2).

The new variables α, which we have to introduce to get a relativistic wave equation linear in W, give rise to the spin of the electron. From the general principles of quantum mechanics one can easily deduce that these variables α give the electron a spin angular momentum of half a quantum and a magnetic moment of one Bohr magneton in the reverse direction to the angular momentum. These results are in agreement with experiment. They were, in fact, first obtained from the experimental evidence provided by spectroscopy and afterwards confirmed by the theory.

The variables α also give rise to some rather unexpected phenomena concerning the motion of the electron. These have been fully worked out by Schrödinger. It is found that an electron which seems to us to be moving slowly, must actually have a very high frequency oscillatory motion of small amplitude superposed on the regular motion which appears to us. As a result of this oscillatory motion, the velocity of the electron at any time equals the velocity of light. This is a prediction which cannot be directly verified by experiment, since the frequency of the oscillatory motion is so high and its amplitude is so small. But one must believe in this consequence of the theory, since other consequences of the theory which are inseparably bound up with this one, such as the law of scattering of light by an electron, are confirmed by experiment.

There is one other feature of these equations which I should now like to discuss, a feature which led to the prediction of the positron. If one looks at Eq. (1), one sees that it allows the kinetic energy W to be either a positive quantity greater than mc^2 or a negative quantity less than $-mc^2$. This result is preserved when one passes over to the quantum equation (2) or (3). These quantum equations are such that, when interpreted according to the general scheme of quantum dynamics, they allow us the possible results of a measurement of W either something greater than mc^2 or something less than $-mc^2$.

Now in practice the kinetic energy of a particle is always positive. We thus see that our equations allow of two kinds of motion for an electron, only one of which corresponds to what we are familiar with. The other corresponds to electrons with a very peculiar motion such that the faster they move, the less energy they have, and one must put energy into them to bring them to rest.

One would thus be inclined to introduce, as a new assumption of the theory, that only one of the two kinds of motion occurs in practice. But this gives rise to a difficulty, since we find from the theory that if we disturb the electron, we may cause a transition from a positive-energy state of motion to a negative-energy one, so that, even if we suppose all the electrons in the world to be started off in positive-energy states, after a time some of them would be in negative-energy states.

Thus in allowing negative-energy states, the theory gives something which appears not to correspond to anything known experimentally, but which we cannot simply reject by a new assumption. We must find some meaning for these states

An examination of the behaviour of these states in an electromagnetic field shows that they correspond to the motion of an electron with a positive charge instead of the usual negative one—what the experimentors now call a positron. One might, therefore, be inclined to assume that electrons in negative-energy states are just positrons, but this will not do, because the observed positrons certainly do not have negative-energies. We can, however, establish a connection between electrons in negative-energy states and positrons, in a rather more indirect way.

We make use of the exclusion principle of Pauli, according to which there can be only one electron in any state of motion. We now make the assumptions that in the world as we know it, nearly all the states of negative energy for the electrons are occupied, with just one electron in each state, and that a uniform filling of all the negative-energy states is completely unobservable to us. Further, *any unoccupied negative-energy state, being a departure from uniformity, is observable and is just a positron.*

An unoccupied negative-energy state, or *hole*, as we may call it for brevity, will have a positive energy, since it is a place where there is a shortage of negative energy. A hole is, in fact, just like an ordinary particle, and its identification with the positron seems the most reasonable way of getting over the difficulty of the appearance of negative energies in our equations. On this view the positron is just a mirror-image of the electron, having exactly the same mass and opposite charge. This has already been roughly confirmed by experiment. The positron should also have similar spin properties to the electron, but this has not yet been confirmed by experiment.

From our theoretical picture, we should expect an ordinary electron, with positive energy, to be able to drop into a hole and fill up this hole, the energy being liberated in the form of electromagnetic radiation. This would mean a process in which an electron and a positron annihilate one another. The converse process, namely the creation of an electron and a positron from electromagnetic radiation, should also be able to take place. Such processes appear to have been found experimentally, and are at present being more closely investigated by experimenters.

The theory of electrons and positrons which I have just outlined is a self-consistent theory which fits the experimental facts so far as is yet known. One would like to have an equally satisfactory theory for protons. One might perhaps think that the same theory could be applied to protons. This would require the possibility of existence of negatively charged protons forming a mirror-image of the usual positively charged ones. There is, however, some recent experimental evidence obtained by Stern about the spin magnetic moment of the proton, which conflicts with this theory for the proton. As the proton is so much heavier than the electron, it is quite likely that it requires some more complicated theory, though one cannot at the present time say what this theory is.

In any case I think it is probable that negative protons can exist, since as far as the theory is yet definite, there is a complete and perfect symmetry between positive and negative electric charge, and if this symmetry is really fundamental in nature, it must be possible to reverse the charge on any kind of particle. The negative protons would of course be much harder to produce experimentally, since a much larger energy would be required, corresponding to the larger mass.

If we accept the view of complete symmetry between positive and negative electric charge so far as concerns the fundamental laws of Nature, we must regard it rather as an accident that the Earth (and presumably the whole solar system), contains a preponderance of negative electrons and positive protons. It is quite possible that for some of the stars it is the other way about, these stars being built up mainly of positrons and negative protons. In fact, there may be half the stars of each kind. The two kinds of stars would both show exactly the same spectra, and there would be no way of distinguishing them by present astronomical methods.

CHAPTER ONE

Origin of Quantum Theory

1.1 Failure of Classical Ideas

Quantum theory originated with the attempt to account for the observed features of black body radiation (also called cavity radiation). Figure 1.1 shows the spectral distribution of black body radiation; $u_\nu d\nu$ is the energy per unit volume of radiation within the frequency interval ν to $\nu + d\nu$.

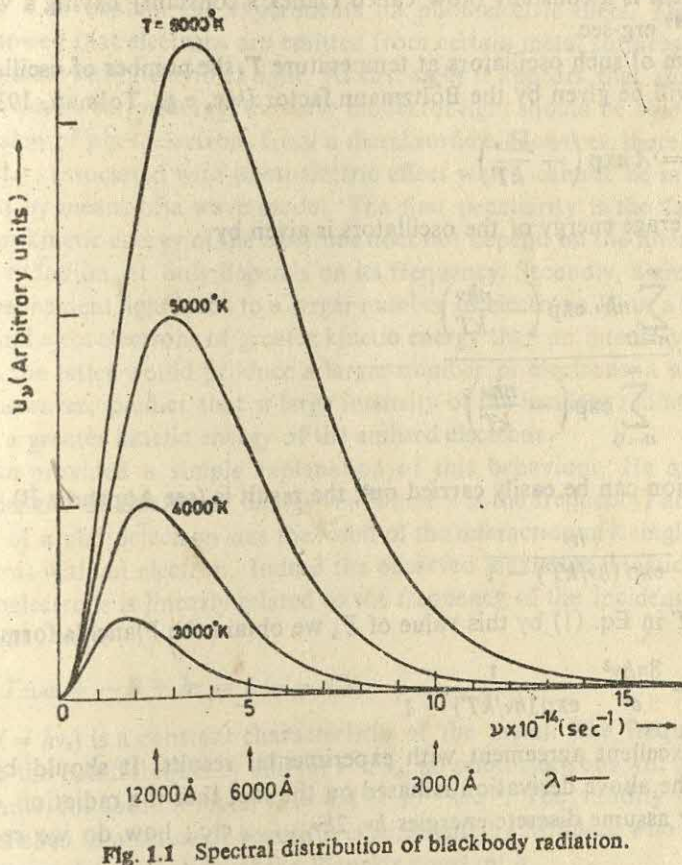

Fig. 1.1 Spectral distribution of blackbody radiation.

It had long been established by Kirchhoff, from very general thermodynamic arguments, that this distribution was independent of the nature of the radiators, i.e., the material of the walls, and depended only on the temperature T. Planck, therefore, started with the simple assumption that the radiators, say the walls, are simple harmonic oscillators. If, as classical physics predicted, from the law of equipartition of energy*, the average energy of the oscillators is kT (k is the Boltzmann constant) then the energy density is given by the Rayleigh-Jeans formula

$$u_\nu = \frac{8\pi}{c^3}\nu^2 kT \tag{1}$$

It can be seen that this formula predicts that u_ν should keep on increasing with ν, in disagreement with the observed distribution shown in Fig. 1.1. A derivation of Eq. (1) is given in Appendix A.

1.2 Planck's Law of Radiation

Planck recalculated the average energy of the oscillators, introducing a drastic assumption that the oscillators can only assume discrete energies $h\nu$, $2h\nu$, . . . , etc.,** where h is a constant (now called Planck's constant) having a value of 6.625×10^{-27} erg-sec.

In a system of such oscillators at temperature T, the number of oscillators of energy $nh\nu$ will be given by the Boltzmann factor (see, e.g., Tolman, 1938)

$$N_n = A\exp\left(-\frac{nh\nu}{kT}\right) \tag{2}$$

Thus, the average energy of the oscillators is given by

$$\overline{\mathcal{E}} = \frac{\sum\limits_{n=0}^{\infty} nh\nu\exp\left(-\frac{nh\nu}{kT}\right)}{\sum\limits_{n=0}^{\infty}\exp\left(-\frac{nh\nu}{kT}\right)} \tag{3}$$

The summation can be easily carried out; the result is (see Appendix B)

$$\overline{\mathcal{E}} = \frac{h\nu}{\exp(h\nu/kT) - 1} \tag{4}$$

Replacing kT in Eq. (1) by this value of $\overline{\mathcal{E}}$, we obtain the Planck's formula

$$u_\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{\exp(h\nu/kT) - 1} \tag{5}$$

which is in excellent agreement with experimental results. It should be mentioned that the above derivation is based on the fact that the radiation oscillators can only assume discrete energies $h\nu$, $2h\nu$, . . . , etc.; how do we reconcile this with experiments on oscillators like a simple pendulum which seem to take continuous energy values? The answer is that the Planck's constant has such a small value that for any 'macroscopic system' the energy $h\nu$ is extremely small and it is usually very difficult to measure such a small quantum of energy. For example, for a classical oscillator with $\nu \sim 1$ sec^{-1}, $h\nu$ is $\sim 6.6 \times 10^{-27}$ ergs which is an extremely small quantity and for all practical purposes we may assume the energy to take continuous values. This is indeed an example of Bohr's correspondence principle according to which the results obtained from quantum theory must go over to the classical results when large number of quanta are involved. It should be pointed out that for light waves $\nu \sim 10^{15}$ sec^{-1} and $h\nu \simeq 6.6 \times 10^{-12}$ erg $\simeq 4$ eV which is a measurable quantity.

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*See, for example, Saha and Srivastava (1965), Rief (1965), etc.

**The original arguments of Planck led him to modify the relation between the entropy of oscillators and internal energy in such a way as to reproduce the experimental results. The implication of the result was appreciated by Planck and he soon produced other derivations explicitly emphasizing discrete energies.

1.3 The Photoelectric Effect

The full impact of Planck's hypothesis was not really apparent until Einstein extended it to explain the experiments on photoelectric effect. These experiments showed that electrons are emitted from certain metal surfaces when they are irradiated with ultraviolet light. At first sight it appears that since electromagnetic waves carry energy, the wave model for light should be able to explain the emission of photoelectrons from a metal surface. However, there are certain peculiarities associated with photoelectric effect which cannot be satisfactorily explained by means of a wave model. The first peculiarity is the fact that the maximum kinetic energy of the electrons does not depend on the intensity of the incident radiation, it only depends on its frequency. Secondly, a greater intensity of the incident light leads to a larger number of electrons. Thus a faint violet light would eject electrons of greater kinetic energy than an intense yellow light although the latter would produce a larger number of electrons; a wave model would, however, predict that a large intensity of the incident radiation would result in a greater kinetic energy of the emitted electrons.

Einstein provided a simple explanation of this behaviour. He argued that light consisted of quanta of energy $h\nu$ (where ν is the frequency) and that the emission of a photoelectron was the result of the interaction of a single quantum (or photon) with an electron. Indeed the observed maximum kinetic energy of the photoelectrons is linearly related to the frequency of the incident radiation and one may write

$$T_{\max} = -B + h\nu = h(\nu - \nu_c) \tag{6}$$

where $B\ (= h\nu_c)$ is a constant characteristic of the metal. The frequency ν_c is known as the cutoff frequency and for $\nu < \nu_c$, no photoelectrons will be emitted. For example, for sodium metal $\nu_c \simeq 4.4 \times 10^{14}$ sec^{-1}. The validity of Eq. (6) was established in a series of beautiful experiments by Millikan who also made the first direct determination of the Planck's constant h.

In making this transition from Planck's *quantized oscillators* to *quanta of radiation*, Einstein had made a very important conceptual transition, namely, he introduced the idea of corpuscular behaviour of radiation. Although Newton had described light as a stream of particles, this view had been completely superseded by the wave picture of light, a picture that culminated in the electromagnetic theory of Maxwell. The revival of the particle picture now posed a severe conceptual problem, one of reconciling wave and particle like behaviour of radiation.

Planck's hypothesis and Einstein's photons fitted well in the Bohr theory* of the hydrogen atom which was the most important point of the success of the early quantum theory. However, there was no direct way of extending Bohr's theory to more complex atoms and in certain crucial experimental observations (such as the anomalous Zeeman effect) the theory proved inadequate.

The major conceptual problem was the one of reconciling the particle and wave-like behaviour of radiation; it soon became apparent that matter also exhibited both types of behaviour. For example, an electron with an accurately measured value of mass and charge could undergo diffraction in a manner similar to that of light waves. We will now give a brief account of some of the other important experimental evidence showing wave-particle duality which led to the development of quantum theory.

1.4 The Compton Effect

We have seen that Einstein's explanation for the photoelectric effect implied that quanta of light (photons) carry definite amount of energy. The Compton effect provided an unambiguous example of a process in which a quantum of radiation carrying energy as well as momentum scatters off an electron.

In 1923 Compton investigated the scattering of X-rays by a block of paraffin and found that the wavelength of the radiation scattered at an angle of 90° is greater than the wavelength of the incident radiation. In other words, the frequency ν' of the scattered wave is smaller than the frequency of the incident wave. Compton was able to explain the result** quantitatively as that of an elastic collision between a photon of energy

$$E = h\nu \tag{7}$$

and momentum†

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*See, e.g., Born (1962).

**According to the classical explanation of the Compton scattering, the electron undergoes oscillatory motion because of the electric field associated with the incident electromagnetic radiation. The accelerated electron emits electromagnetic waves and because of Doppler shifts due to the motion of the electron, the emitted wavelength differs from the wavelength of the incident radiation; however, the classical theory predicts that for a given angle of scattering a continuous range in the value of the scattered wavelength should be found, which is contrary to experimental findings. The details of this analysis are given in Bohm (1951), Sec. 2.9.

†Equation (8) follows from the fact that according to the classical theory, the momentum (per unit volume) associated with the radiation in free space is given by

$$p = \frac{E}{c}$$

where E is the energy density associated with the electromagnetic field (see, e.g., Ghatak, 1977, Chapter 19).

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{8}$$

with an electron. The light quantum imparts some of its energy to the electron and emerges with less energy. Thus the scattered radiation has a lower frequency. The kinematics of this collision process can be worked out on elementary application of the laws of conservation of energy and momentum [see, for example, Ghatak (1977), Chapter 21]. These calculations give the following expression for the shift in the wavelength

$$\Delta\lambda = \frac{2h}{mc}\sin^2 \varphi/2 \tag{9}$$

where φ is the angle of scattering of the light quantum [see Figs. 1.2(a) and (b)].

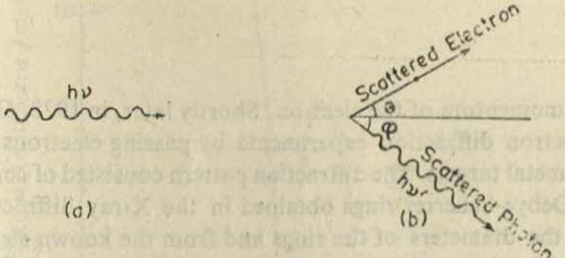

Fig. 1.2 The Compton scattering of a photon: (*a*) shows the incidence of a photon (of frequency ν) on an electron at rest, (*b*) shows the scattered photon (having a reduced frequency ν′) propagating along a direction which makes an angle φ with the original direction; the electron also acquires a momentum.

Further evidence of the validity of the above theory was provided by the experiments carried out by Compton and Simon who studied the scattering of X-rays through supersaturated water vapour. In the scattering process, the recoil electrons formed tracks of condensed droplets; however, the light quantum did not leave any track. Now if the light quantum undergoes another Compton scattering then from the track of the second recoil electron one can determine the path of the light quantum by simply joining the line of the starting points of the two recoil electrons. Although there was considerable uncertainty in the analysis of the experimental data (because of the presence of many tracks) Compton and Simon could establish agreement between the theoretical results and experimental data.

1.5 Wave Nature of Matter

Experiments by Wilson with his cloud chamber had clearly shown the particle like behaviour of alpha and beta particles. These are emitted by radioactive elements and when they pass through supersaturated vapour, they form tracks of condensed droplets. For the alpha particles, these tracks are nearly straight lines; however, for the electrons, the tracks are irregularly curved. The existence of continuous tracks suggest that the emissions from the radioactive substance can be regarded as minute particles moving with high speed. Further, the fact that the electrons could be deflected by electric and magnetic fields and also the fact that one could accurately determine the ratio of their charge to mass suggest very strongly that electrons are particles. This view remained unchallanged for a number of years.

At this stage one could ask if matter may not show wave-like behaviour also just as light exhibited corpuscular and wave-like behaviour: In 1925, de Broglie proposed just such a hypothesis and argued that the relation given by Eq. (8), between wavelength and momentum applied for electrons as well.

In 1927, Davisson and Germer studied the diffraction of electrons from single crystals* of nickel and showed that the diffraction patterns could be explained if the electrons were assumed to have a wavelength given by the de Broglie relation

$$\lambda = \frac{h}{p} \tag{10}$$

where p is the momentum of the electron. Shortly later, in 1928, G.P. Thomson carried out electron diffraction experiments by passing electrons through thin polycrystalline metal targets. The diffraction pattern consisted of concentric rings similar to the Debye-Scherrer rings obtained in the X-ray diffraction pattern. By measuring the diameters of the rings and from the known structure of the crystals, Thomson calculated the wavelength associated with the electron beam which was in agreement with the de-Broglie relation.

A more modern example of the wave-like behaviour of material particles is the study of scattering by nuclei. The experiment is schematically shown in Fig. 1.3, and in Fig. 1.4 we have shown a typical variation of intensity of scattered α-particles with the scattering angle. A typical diffraction pattern is seen with successive maxima spaced at about 13°.

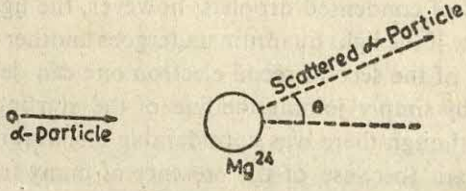

Fig. 1.3 The elastic scattering of an α-particle by a Mg^{24} nucleus; θ is the angle of scattering.

One can assume, as a first approximation, that the nucleus acts like a 'black' disc, i.e., all α-particles whose centres come within a distance a of the centre of the magnesium nucleus. will be absorbed. (We expect a to be approximately the sum of the radii of the α-particle and of the Mg^{24} nucleus). In that case, the

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*The diffraction pattern consisted of spots similar to the Laue spots obtained in the X-ray diffraction pattern.

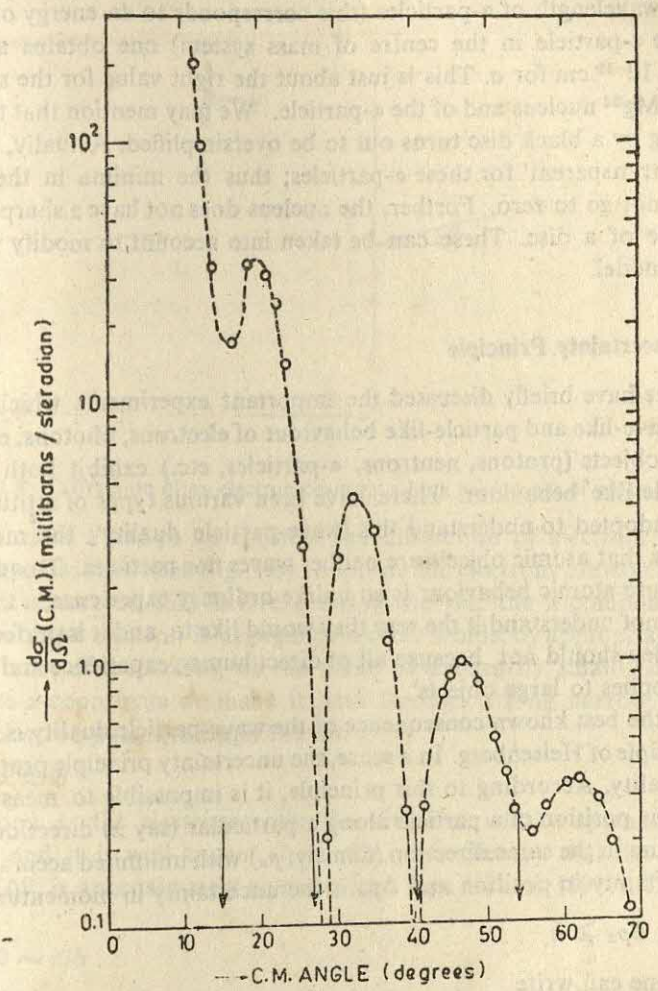

Fig. 1.4 The intensity variation of 42 MeV α-particles (the differential cross-section) elastically scattered from Mg^{24} (adapted from I.M. Naquib and J.S. Blair, *Phys. Rev.* **165**, 1250, 1968).

problem is the same as that of diffraction* of light by an opaque disc and successive maxima will be spaced at about

$$\Delta\theta \simeq \frac{1.22\lambda}{2a} = \frac{1.22h}{2pa} \tag{11}$$

---

*The diffraction pattern by an opaque disc can be approximately calculated by using Babinet's principle; see, for example, Ghatak (1977), Chapter 16. The intensity distribution would be approximately proportional to

$$\left| 1 - e^{-i\pi/2} \frac{2J_1(V)}{V} \right|^2$$

where $V = (2\pi/\lambda)a \sin\theta$, a being the radius of the disc, θ is the angle of scattering and $J_1(V)$ represents the Bessel function of first order.

where p is the momentum of the alpha particle. Using a value of about 2.6×10^{-13} cm for the wavelength of α-particles (this corresponds to an energy of about 31 MeV of the α-particle in the centre of mass system) one obtains a value of about 4.9×10^{-13} cm for a. This is just about the right value for the sum of the radii of the Mg^{24} nucleus and of the α-particle. We may mention that the picture of scattering by a black disc turns out to be oversimplified. Actually, nuclei are somewhat 'transparent' for these α-particles; thus the minima in the intensity pattern do not go to zero. Further, the nucleus does not have a sharp boundary in the sense of a disc. These can be taken into account to modify the simple diffractive model.

1.6 The Uncertainty Principle

In above we have briefly discussed the important experiments which demonstrate the wave-like and particle-like behaviour of electrons, photons, etc. Indeed all atomic objects (protons, neutrons, α-particles, etc.) exhibit both wave-like and particle-like behaviour. There have been various types of attitudes which have been adopted to understand this 'wave-particle duality'; the most widely held view is that atomic objects are neither waves nor particles. To quote Feynman, 'Because atomic behaviour is so unlike ordinary experience, . . . even the experts do not understand it the way they would like to, and it is perfectly resonable that they should not, because all of direct human experience and of human intuition applies to large objects'.

Perhaps the best known consequence of the wave-particle duality is the uncertainty principle of Heisenberg. In a sense, the uncertainty principle protects wave-particle duality. According to this principle, it is impossible to measure simultaneously the position of a particle along a particular (say x) direction and also its momentum in the same direction (namely, p_x) with unlimited accuracy*. If Δx is the uncertainty in position and Δp_x is the uncertainty in momentum then

$$\Delta x \, \Delta p_x \gtrsim h \tag{12}$$

Similarly, one can write

$$\Delta y \, \Delta p_y \gtrsim h \quad \text{and} \quad \Delta z \, \Delta p_z \gtrsim h \tag{13}$$

In order to understand the inherent uncertainties associated with simultaneous

---

*There has been an unending debate about the interpretation of the uncertainty principle and there are those who would claim that this statement is wrong. Alfred Lande [see his article on 'Quantum Fact and Fiction III', *American Journal of Physics*, 37, p. 541 (1969)] is one who takes an extreme position in this debate and has even argued that there is no wave-particle duality and electron diffraction and light diffraction can be explained by quite different arguments. As we have emphasized, diffraction theories of particles play an important role in modern physics and one would find it sterile for scientific progress to invoke entirely different arguments for analogous behaviour of matter and light. There are, however, a whole range of views on the question of interpretation of quantum mechanics, especially on the role of the observer and measurement, and the subject is not a closed one. For a readable account of the early history of this debate, see Jammer (1966).

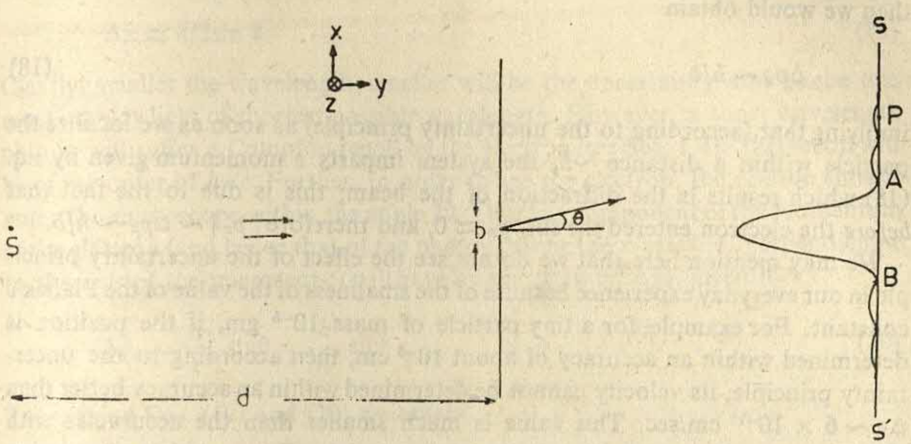

Fig. 1.5 Diffraction of an electron beam by a long narrow slit of width b.

measurements of x and p_x we consider the diffraction of electrons by a long narrow slit of width b (see Fig. 1.5). Suppose the electrons are coming from a very distant source so that before entering the slit, the x-component of the momentum of the electron is negligible (in other words, by appropriately choosing the distance of the source, we can make p_x arbitrarily small). In order to measure the x-coordinate we make it pass through a long narrow slit. Thus, when the electron passes through the slit

$$\Delta x \approx b \tag{14}$$

Now, as soon as the electrons enter the slit there will be spreading due to diffraction and it is well-known (from the wave theory) that the diffraction spreading, $\Delta\theta$, is approximately given by [see, e.g., Ghatak (1977), Chapters 15 and 16]:

$$\Delta\theta \sim \lambda/b \tag{15}$$

Thus the electron acquires a momentum in the x-direction which is given by

$$\Delta p_x \sim p_x \sim p\Delta\theta \sim p\frac{\lambda}{b} \tag{16}$$

Using Eqs. (14) and (16) one gets

$$\Delta x\, \Delta p_x \sim h \tag{17}$$

where we have used the de Broglie relation (Eq. 10). Thus, if we make b (and hence Δx) smaller, there will be more diffraction and hence a greater uncertainty in p_x which is consistent with the uncertainty principle. It may be mentioned that it will be incorrect to say that $\Delta p_x \approx 0$ and $\Delta x \approx b$ because Δp_x was small *before* the electron entered the slit. After entering the slit, Δp_x is no more zero; the slit imparts momentum in the x-direction.

The uncertainty relation given by Eq. (17) for which a more rigorous derivation will be given in Sec. 2.6, is called Heisenberg's uncertainty relation. It should be noted that if we use Eq. (11) and the uncertainty principle [Eq. (17)] then we would obtain

$$\Delta p_x \sim h/b \tag{18}$$

implying that (according to the uncertainty principle) as soon as we localize the particle within a distance $\sim b$, the system imparts a momentum given by Eq. (18) which results in the diffraction of the beam; this is due to the fact that *before* the electron entered the slit, $p_x \approx 0$, and therefore $|p_x| \sim \Delta p_x \sim h/b$.

We may mention here that we do not see the effect of the uncertainty principle in our everyday experience because of the smallness of the value of the Planck's constant. For example, for a tiny particle of mass 10^{-5} gm, if the position is determined within an accuracy of about 10^{-5} cm, then according to the uncertainty principle, its velocity cannot be determined within an accuracy better than $\Delta v \sim 6 \times 10^{-17}$ cm/sec. This value is much smaller than the accuracies with which one can determine the velocity of the particle. For a particle of a greater mass Δv will be even smaller. Indeed, had the value of Planck's constant been much larger, the world would have been totally different. In a beautifully written book, Gamow (1940) has discussed what our world would be like if the Planck's constant had a value of 1 erg-sec so that the effect of the uncertainty principle would be apparent to our sense of perception.

Another illustration of the uncertainty relation can be had by considering the measurement of position by a microscope. It is well-known that a microscope cannot resolve two points which are separated by a distance which is $\lesssim \lambda/(2 \sin \theta)$, where λ is the wavelength of the radiation and θ is the angular aperture of the microscope (see Fig. 1.6). In other words, the uncertainty in the location of an

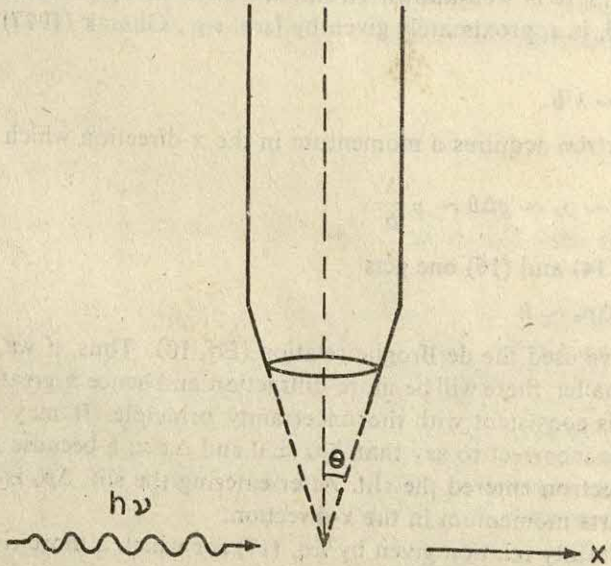

Fig. 1.6 Determination of the position of an electron by means of a γ-ray microscope.

electron would be given by

$$\Delta x \approx \lambda/2\sin\theta \tag{19}$$

Clearly, smaller the wavelength, smaller will be the uncertainty and hence one must employ light of shortest possible wavelength. However, a short wavelength photon will suffer a Compton recoil by the electron (see Sec. 1.4). This recoil will be of tne order of $h\nu/c$. Further, in order to see the electron, the photon should enter the microscope within the angle 2θ. Thus the component of the momentum of the electron (and hence that of the photon) along the x-axis (i.e., perpendicular to the axis of the microscope) will have an uncertainty, Δp_x, given by

$$\Delta p_x \sim \frac{h\nu}{c}\sin\theta = \frac{h}{\lambda}\sin\theta \tag{20}$$

Thus, using Eqs. (19) and (20) we obtain

$$\Delta x \Delta p_x \sim h \tag{21}$$

We conclude this section by quoting Max Born: 'Physicists of today have learned that not every question about the motion of an electron or a photon can be answered, but only those questions which are compatible with the uncertainty principle.'

1.7 Some Interesting Applications of Uncertainty Principle

In this section we will use the uncertainty principle to show the finite size of atoms; however, before we do so we consider a simpler problem, namely a linear harmonic oscillator for which the total energy is given by

$$E = \frac{p_x^2}{2m} + \tfrac{1}{2} m\omega^2 x^2 \tag{22}$$

We assume the particle to be confined to a region $\sim a$; i.e.,

$$x \sim \Delta x \sim a \tag{23}$$

and, according to uncertainty principle

$$p_x \sim \Delta p_x \sim \frac{\hbar}{2a} \tag{24}$$

where* $\hbar \equiv h/2\pi$. thus

$$E \approx \frac{\hbar^2}{8ma^2} + \tfrac{1}{2} m\omega^2 a^2 \tag{25}$$

The lowest energy state of the oscillator (which is called the ground state) will correspond to the minimum value of E for which $dE/da = 0$. Thus

$$\frac{dE}{da} = -\frac{\hbar^2}{4ma^3} + m\omega^2 a = 0$$

---

*We are using the uncertainty relation $\Delta x \Delta p_x \approx \frac{1}{2}\hbar$ (see Sec. 2.6) just to get the right result! Arguments based on uncertainty principle are expected to give only 'rough estimates'.

giving

$$a \approx \left[\frac{\hbar}{2m\omega}\right]^{\frac{1}{2}} \tag{26}$$

The minimum energy is given by

$$E \simeq \frac{\hbar^2}{8m} \cdot \frac{2m\omega}{\hbar} + \tfrac{1}{2}m\omega^2 \frac{\hbar}{2m\omega} = \tfrac{1}{2}\hbar\omega \tag{27}$$

which is indeed the gound state energy of the linear harmonic oscillator (See Sec. 3.6.3). The quantity $\frac{1}{2}\omega\hbar$ is known as the *zero point energy* and is a consequence of the uncertainty principle. We must mention that the results obtained by using uncertainty principle can only predict the order of magnitude of the quantity; in our analysis, we have used the constants in such a way that the final result is exact! In Sec. 3.6.3 we will show that for an oscillator in the ground state the probability that the particle lies between x and $x + dx$ is given by

$$P(x)\,dx = \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 x^2}\,dx \quad \text{where} \quad \alpha = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} \tag{28}$$

Thus the particle is localized in a distance of the order of $(\hbar/m\omega)^{1/2}$ which is consistent with Eq. (26).

We next use the uncertainty principle for determining the size of the atom. We consider the simplest atom, namely, the hydrogen atom which consists of an electron and a proton. The logic of the argument is the same as for the linear harmonic oscillator: we assume that the electron is confined to a region $\sim a$, then according to the uncertainty principle* $p \sim \Delta p \sim \hbar/a$, where $\hbar \equiv h/2\pi$. Thus

$$\text{Kinetic energy} = \frac{p^2}{2m} \simeq \frac{\hbar^2}{2ma^2}$$

The electrostatic potential energy** is $-e^2/a$; therefore the total energy is given by

$$E \simeq \frac{\hbar^2}{2ma^2} - \frac{e^2}{a} \tag{29}$$

The ground state of the atom will correspond to a minimum value of E for which dE/da must be equal to zero. Thus

$$\frac{dE}{da} = -\frac{2\hbar^2}{2ma^3} + \frac{e^2}{a^2} = 0$$

---

*Once again, we are choosing the constants in such a way so as to get the exact results. Further, the uncertainty principle relates Δx to Δp_x, Δy to Δp_y, etc., and

$$p^2 = p_x^2 + p_y^2 + p_z^2 \sim (\Delta p_x)^2 + (\Delta p_y)^2 + (\Delta p_z)^2 \sim \frac{\hbar^2}{a^2}$$

the result representing only the correct order.

**We are using the cgs units; in mks units the expression is $-q^2/4\pi\varepsilon_0 a$, where q is the electronic charge in mks units.

or $$a = a_0 = \hbar^2/me^2 \simeq \tfrac{1}{2}\,\mathring{A} = \tfrac{1}{2} \times 10^{-8}\ \text{cm} \tag{30}$$

where a_0 represents the minimum value of a. Thus the finite size of the atom is due to the uncertainty principle. Equation (30) tells us that the atomic dimensions are of the order of Angstroms which is indeed correct. The minimum energy is given by

$$E = \frac{\hbar^2}{2ma_0^2} - \frac{e^2}{a_0} = -\frac{me^4}{2\hbar^2} \simeq -13.6\ \text{eV} \tag{31}$$

which is indeed the ground state energy of the hydrogen atom (see Sec. 5.3). Considerations for a 2-electron atom are discussed in Problem 1.3.

Feynman writes [quoted from Feynman *et al.* (1965)] 'So we now understand why we do not fall through the floor . . . . In order to squash the atoms close together, the electrons would be confined to a smaller space and, by the uncertainty principle, their momenta would have to be higher on the average, and that means high energy; the resistance to atomic compression is a quantum mechanical effect . . . .'

1.8 The Probabilistic Interpretation of Matter Waves

In Sec. 1.6 we have seen that if an electron passes through a slit of width b, then the momentum imparted in the x-direction (which is along the width of the slit) is $\sim h/b$. The question arises whether we can predict the trajectory of an individual electron. The answer is no. We cannot say where an individual electron will land up on the screen; we can only predict the probabilities of arrival of the electron in a certain region of the screen. We may, for example, say that the probability for the arrival of the electron in the region lying between the points A and P (see Fig. 1.5) is 0.10. This would imply that if the experiment was carried out with a large number of electrons, about 10% of them would land up in the region AP; but the fate of an individual electron can never be predicted. It should be mentioned that if we place a detector on the screen, then it will always record one electron or none and never half of an electron. This essentially implies the corpuscular nature of the electron. However, the probability distribution is the same as predicted by the wave theory (see Problems 2.13 and 2.14) and therefore if one performs an experiment with a large number of electrons (as is indeed the case in most experiments) the intensity distribution recorded on the screen is the same as predicted by the wave theory.

In order to explicitly show that the diffraction is not a many photon phenomenon, Taylor in 1909 carried out a beautiful experiment which consisted of a box with a small lamp which casts the shadow of a needle on a photographic plate. The intensity of the light was so weak that between the needle and the photographic plate, it was almost impossible to find two photons (see Problem 1.7). In fact, to get a good fringe pattern Taylor made an exposure lasting for several months. The diffraction pattern, obtained on the photographic plate, was the same as predicted by the wave theory.

The corpuscular nature of radiation and the fact that one cannot predict the trajectory of an individual photon can be seen from Fig. 1.7 which consists of series of photographs showing the quality of pictures obtainable from various number of photons. The photograph clearly shows that the picture is built up by the arrival of concentrated packets of energy and the point at which a particular photon will arrive is entirely a matter of chance. The figure also shows that the photograph is featureless when a small number of photons are involved and as the number of photons reaching the photographic plate increases, the intensity distribution becomes the same as would be predicted by the wave theory.

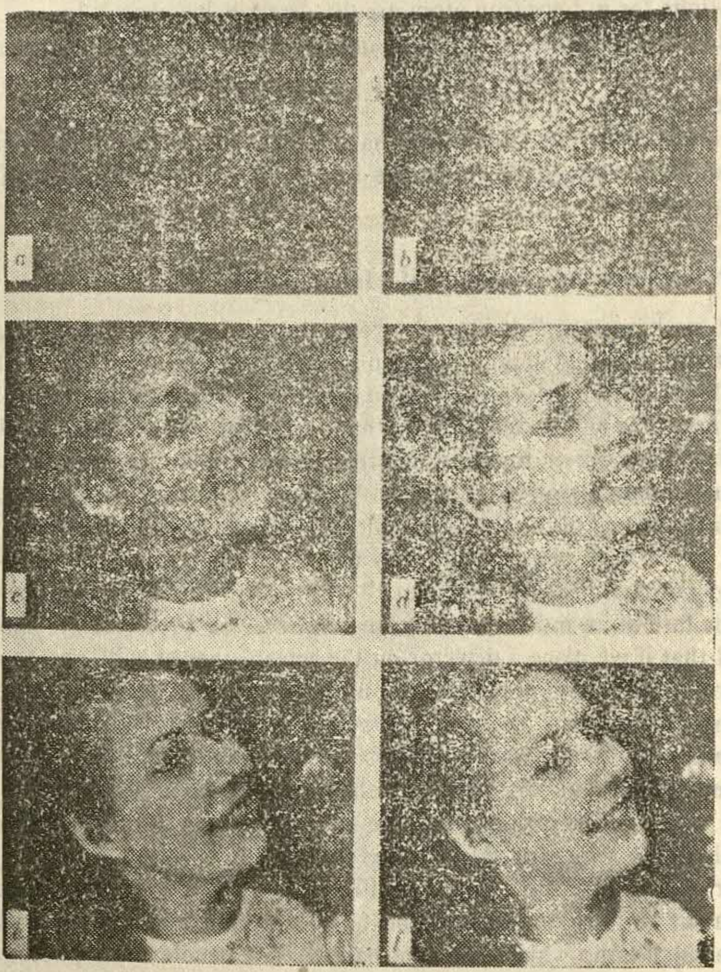

Fig. 1.7 Photographs showing the quality of a picture obtainable from various number of photons, (a), (b), (c), (d), (e) and (f) correspond to 3×10^3 photons, 1.2×10^4 photons, 9.3×10^4 photons, 7.6×10^5 photons, 3.6×10^6 photons and 2.8×10^7 photons respectively. (From A Rose, Quantum Effects in Human Vision, *Advances in Biological and Medical Physics*, Vol. V, Academic Press, 1957).

1.9 An Understanding of Interference Experiments

We next consider the interference experiment involving the Michelson interferometer in which a light beam is partially reflected by a beam splitter and the resulting beams are made to interfere (see Fig. 1.8). According to Dirac (1958) '. . . we describe the photon as going partly into each of the two components into which the incident beam is split. The photon is then, as we may say, in a translational state given by the superposition of the two translational states associated with the two components . . . '. For a photon to be in a definite translational state it need not be associated with one single beam of light, but may be associated with two or more beams of light, which are the components into which one original beam has been split. In the accurate mathematical theory each translational state is associated with one of the wave functions of ordinary wave optics, which may describe either a single beam or two or more beams into which one original beam has been split. These translational states can be superposed in a manner similar to the one employed while considering the interference of two beams. Thus, each photon goes partly into each of the two components and interferes only with itself. If we try to determine the fate of a single photon by measuring the energy in one of the components then Dirac argues: 'The result of such a determination must be either a whole photon or nothing at all. Thus the photon must change suddenly from being partly in one beam and partly in the other to be entirely in one of the beams. This sudden change is due to the disturbance in the translational state of the photon which the observation necessarily makes. It is impossible to predict in which of the two beams the photon will be found. Only the probability of either result can be calculated . . . . Our description of the photon allows us to infer that, *after* such an energy measurement, it would not be possible to bring about any interference effects

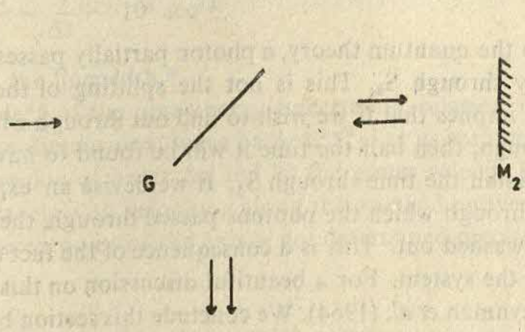

Fig. 1.8 Outline of the Michelson interferometer experiment to obtain an interference pattern. G represents a beam splitter, M_1 and M_2 represent plane mirrors.

between the two components. So long as the photon is partly in one beam and partly in the other, interference can occur when the two beams are superposed, but this possibility disappears when the photon is forced entirely into one of the beams by an observation'.

In a similar manner we may consider the two hole interference experiment similar to that performed by Young. The experimental arrangement is shown in Fig. 1.9 where a weak light source S_0 illuminates the hole S and the light beams emerging from the holes S_1 and S_2 produce the interference pattern on the screen PP′. The intensity is assumed to be so weak that in the region between the planes AB and PP′ there is almost never more than one photon (see Problem 1.7). Individual photons are counted by a detector on the screen PP′ and a study of the count pattern will show that although there is no way to predict the location of the appearance of a particular count, the frequency of occurrence of counts in any small region will be proportional to the intensity in that region as predicted by wave theory. Thus the wave theory predicts the distribution of energy in an interference pattern but not its arrival in discrete units.

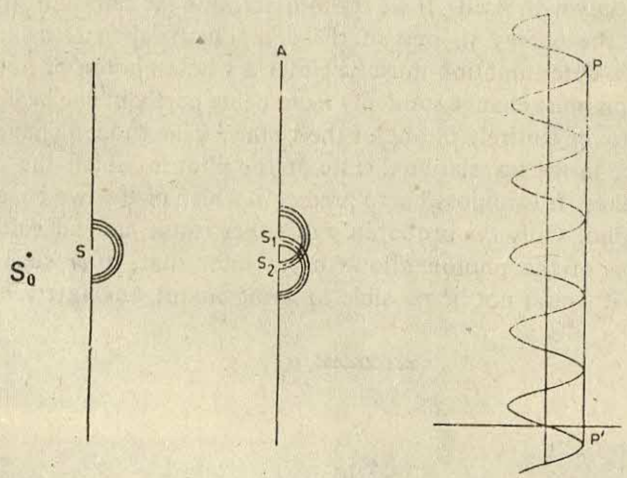

Fig. 1.9 Young's double hole experimental arrangement for obtaining the interference pattern. S_0 represents a point source.

According to the quantum theory, a photon partially passes through the hole S_1 and partially through S_2. This is not the splitting of the photon into two halves but only implies that if we wish to find out through which hole the photon passed through, then half the time it will be found to have passed through the hole S_1 and half the time through S_2. If we devise an experiment to determine the hole through which the photons passed through, then the interference pattern will be washed out. This is a consequence of the fact that measurement always disturbs the system. For a beautiful discussion on this point, the reader is referred to Feynman *et al.* (1964). We conclude this section by quoting Margenau (1961) 'the physicist, while still fond of mechanical models wherever they are available and useful, no longer regards them as the ultimate goal of all scientific description; he recognizes situations where the assignment of a simple model, especially a mechanical one, no longer works and where he feels called upon to proceed directly under the guidance of logical and mathematical considerations and at times with the renunciation of the visual aspects which classical physics would carry into the problem'.

1.10 The Time-Energy Uncertainty Relation

We have seen that if a measurement of position is made with accuracy Δx, and if a measurement of the x-component of momentum is made simultaneously with accuracy Δp_x, then

$$\Delta x \, \Delta p_x \gtrsim h \tag{32}$$

In an analogous manner there exists a time-energy uncertainty relation according to which

$$\Delta E \, \Delta t \gtrsim h \tag{33}$$

However, the physical interpretation of Eq. (33) is quite different from that of Eq. (32). The time-energy uncertainty relation implies that an energy determination that has an accuracy ΔE must occupy at least a time interval $\Delta t \sim h/\Delta E$; thus if a system is in a certain state for not longer than Δt, the energy of the system in that state is uncertain by at least $\Delta E \sim h/\Delta t$, since the maximum time available for energy determination is Δt. For example, the average time that an atom retains excess excitation energy before re-emitting it in the form of a photon is $\sim 10^{-8}$ sec (this time is known as the mean life-time of the excited state). This imposes a limitation on the precision with which the excitation energy can be determined and the uncertainty is given by

$$\Delta E \sim \frac{h}{\Delta t} \sim \frac{6 \times 10^{-27}\ \text{erg}\cdot\text{sec}}{10^{-8}\ \text{sec}} \sim 6 \times 10^{-19}\ \text{ergs} \tag{34}$$

or,

$$\Delta E \sim 4 \times 10^{-7}\ \text{eV} \tag{35}$$

Since $\Delta E = h\Delta\nu$, we get

$$\Delta\nu = \frac{\Delta E}{h} \sim \frac{1}{\Delta t} \sim 10^{8}\ \text{sec}^{-1} \tag{36}$$

which is known as the linewidth.*

A second example** of the time-energy uncertainty relation is provided by the motion of a one-dimensional wave packet.*** Let us assume that the wave packet occupies a region of order Δx and let the group velocity be v. The wave packet therefore travels with velocity v along the x-axis; however, the instant at which it passes a given point of the axis is not determined precisely, but carries an uncertainty

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*For a rigorous discussion on linewidth see Problem 22.3.

**Another example occurs in the discussion on transition probability—see Sec. 20.2.

***The definition of a wave packet and how it propagates is discussed in the next chapter.

$$\Delta t \approx \frac{\Delta x}{v} \tag{37}$$

Now, if a wave packet is localized to a region Δx, then the spread in the momentum Δp will be given by

$$\Delta p \gtrsim \frac{h}{\Delta x} \tag{38}$$

or,

$$\Delta x \gtrsim \frac{h}{\Delta p} \tag{39}$$

Substituting in Eq. (37) we obtain

$$\Delta t \gtrsim \frac{h}{v \Delta p}$$

or,

$$\Delta t \, v \, \Delta p \gtrsim h \tag{40}$$

But

$$\Delta E \approx \frac{\partial E}{\partial p} \Delta p = v \, \Delta p \tag{41}$$

Thus

$$\Delta E \, \Delta t \gtrsim h \tag{42}$$

The above relation tells us that if ΔE represents the spread in the energy of a particle then the uncertainty in the instant of passage of the particle through a point will be given by

$$\Delta t \gtrsim \frac{h}{\Delta E} \tag{43}$$

We end this section by mentioning, briefly, that there also exists an uncertainty relation for angle variables. This uncertainty relation is often written in the form*

$$\Delta L_z \, \Delta\varphi \gtrsim h \tag{44}$$

where L_z denotes the z-component of the angular momentum. Equation (44) implies that if the angular position of a particle in an orbit is precisely measured, then the knowledge of the component of the angular momentum perpendicular to the plane of the orbit is completely lost. However, the uncertainty relation in the form given by Eq. (44) is not correct. This is obvious from the fact that $\Delta\varphi$ must be finite, since φ has a finite range of extent 2π. Hence, as ΔL_z tends to zero the left hand side of Eq. (44) tends to zero and a contradiction results.

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*See, for example, Schiff (1968), Sec. 3.

Careful analyses of this uncertainty relation has been carried out by several workers.*

Several thought experiments on the uncertainty principle have been discussed by Kothari.** An edited book by Price and Chissick (1977) discusses many aspects of the uncertainty principle.

1.11 Necessity of Quantum Theory

It may be seen from the foregoing discussion that significant quantum effects are generally observed only in the microscopic world of atoms. However, the import of quantum theory is far-reaching. In his theoretical model of the hydrogen atom, Bohr had introduced the radical notion that the atom can only exist in discrete energy states, the lowest such state being the normal state of the atom.

A little thought will convince us that the hypothesis of discrete states explains the unusual stability of atoms and indeed of all matter (see Problem 1.8). A carbon atom, for example, remains a carbon atom after collisions since infinitesimal variations of structure of the atom are not permissible in the quantum theory. Thus, the very permanence of matter is a concept that is alien to classical ideas and requires a fundamental change of theoretical structure.***

1.12 The Stern-Gerlach Experiment****

Experiments of Franck and Hertz had indicated the correctness of the Bohr hypothesis of quantized energy states. However, the most dramatic and direct evidence for quantization was provided by the experiment of Stern and Gerlach. In a sense, this is the prototype of many thought experiments and we conclude this chapter with a discussion of its basic principles.

The aim of Stern and Gerlach was to measure the magnetic moment of atoms or molecules. A simple diagram of their experimental arrangement is shown in Fig. 1.10(a). Atoms of silver from a hot oven *O* issue out of a narrow slit S_1 and are further collimated by slits S_2 and S_3. The beam of silver atoms then passes through a region of magnetic field between specially designed pole tips which give a strong inhomogeneous magnetic field. Looking into the beam, the tips appear as shown in Fig. 1.10(b). The beams then condense on the detector D. The apparatus is evacuated by a pump ass hown.

The atoms, behaving like magnets of moment μ, will be acted upon by a force

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*See, for example, D. Judge, 'On the Uncertainty Relation for L_z and φ', *Physics Letters*, 5, (1963), p. 189; M. Bouten, N. Maene and P. Van Leuven, 'On the Uncertainty Relation for Angular Variables', *Il Nuovo Cimento*, 37, (1965), p. 1119; M.M. Nieto, 'Angular Momentum Uncertainty Relation and the Three-Dimensional Oscillator in the Coherent States', *Physical Review Letters*, **18**. (1967), p. 182.

**D. S. Kothari, 'Three Elementary Examples of the Uncertainty Principle', *Phil. Mag.*, 27, (1939), p. 62.

***For a beautiful presentation of these ideas, see V. F. Weisskopf, *Science*, **149**, 1181 (1965).

****The Stern-Gerlach experiment is also discussed in Secs. 8.5 and 9.4.

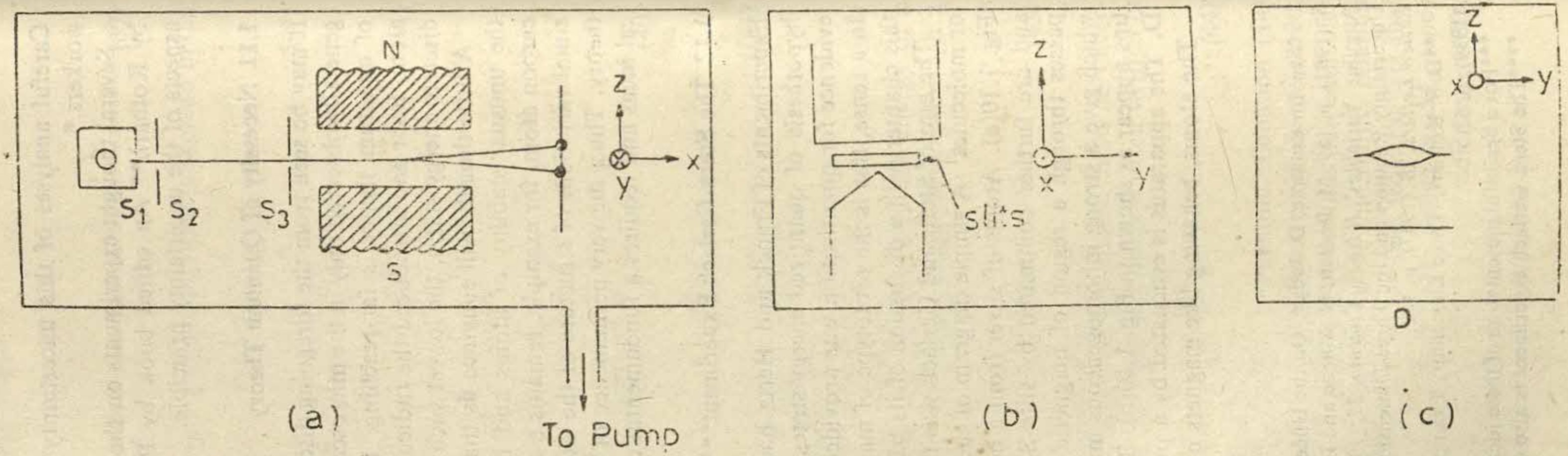

Fig. 1.10 (a) The Stern-Gerlach set up; (b) The tips of the magnet which produce a strong inhomogeneous field; (c) The upper and lower curves show the record of the detector in the presence and absence of the inhomogeneous magnetic field.

which is essentially in the z-direction as indicated, its magnitude being (see Sec. 9.4).

$$F_z = \mu \cos\theta \, \frac{\partial B}{\partial z} \tag{45}$$

where θ is the angle between μ and $\hat{z}$. Travelling a distance l through the region of the magnetic field, the beam will experience a deflection z given by

$$z = \tfrac{1}{2}\left(\frac{F_z}{M}\right) t^2 = \tfrac{1}{2}\,\frac{\mu\cos\theta}{M}\left(\frac{\partial B}{\partial z}\right)\left(\frac{l}{v}\right)^2 \tag{46}$$

where M is the mass and v is the velocity of the atoms. The atomic velocities, although not unique, will range around a mean value $\bar{v}$ determined by the temperature of the oven.

In the absence of the magnetic field, the beam, defined by the slits, forms a narrow line. When the field is turned on, the line ought to widen continuously in the z-direction, the widest deflections recorded by atoms whose magnetic moments are aligned along or opposite the z-direction. Instead, the detector recorded a two-line pattern showing that the silver beam had split into two on passing through the inhomogeneous field [Fig. 1.10(c)]. In other words, the magnetic moment of silver appeared to be oriented in either of two directions, a phenomenon that demonstrated space quantization. Since, in classical theory, the magnetic moment of the atom is proportional to its angular momentum, this result may also be interpreted as evidence of the quantization of angular momentum.

The Stern-Gerlach experiment was, on the face of it, a triumphant vindication of Bohr's postulate on the quantization of angular momenta. Similarly, the electron diffraction experiments verified the de Broglie hypothesis on matter waves. But there were several unsatisfactory features. The rules of these models appeared *ad hoc*; besides they were unable to give a quantitative account of many phenomena such as dispersion of light and intensities of spectral lines. Above all, a mathematical apparatus that gives a unified and coherent description of both the particle and wave aspects of matter was necessary. It soon evolved out of two apparently distinct formulations, later shown to be equivalent: the method of Matrix Mechanics and that of Wave Mechanics.

PROBLEMS*

PROBLEM 1.1

An electron of energy 200 eV is passed through a circular hole of radius 10^{-4} cm. What is the uncertainty introduced in the angle of emergence?

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*In solving the problems, assume the uncertainty products ($\Delta x\ \Delta p_x$ or $\Delta E\ \Delta t$) to be of the order $\hbar(=h/2\pi)$ (see Sec. 2.6). The use of $\hbar$ instead of h gives a better estimate of the result. In any case, the results obtained cannot be expected to be accurate; they would only give the correct order.

PROBLEM 1.2

In continuation of the previous problem, what would be the corresponding uncertainty for a 0.1 g lead ball thrown with a velocity 10^3 cm/sec through a hole 1 cm in radius?

PROBLEM 1.3

Use the uncertainty principle to estimate the energy of the ground state of a two-electron atom of nuclear charge Ze. (*Hint*: Use a method similar to that used in Sec. 1.7.)

PROBLEM 1.4

Yukawa had suggested the existence of a massive meson to explain nuclear force. Using the uncertainty principle; derive a relation between the range of the force and the mass of the meson.

PROBLEM 1.5

In a series of experiments on the determination of the mass of the ω^0 particle, the results showed a variation of $\pm 20\ m_e$, where m_e is the electron mass. What can you say about the lifetime of these particles?

PROBLEM 1.6

Calculate the uncertainty in the momentum of a proton which is confined to a nucleus of radius equal to 10^{-13} cm. From this result, estimate the kinetic energy of the proton inside the nucleus and the strength of the nuclear interaction. What would be the kinetic energy for an electron if it had to be confined within a similar nucleus?

PROBLEM 1.7

Let a source (with $\lambda = 5 \times 10^{-5}$ cm) of power 1W be used in the experimental arrangement shown in Fig. 1.9. (a) Calculate the number of photons that are being emitted by the source per second. (b) Assume that the radii of the holes S, S_1 and S_2 to be 0.02 cm and $S_0S = SS_1 = SS_2 = 100$ cm and the distance between the planes AB and PP′ to be also 100 cm. Show that in the region between the planes AB and PP′ one can almost never find two photons.

PROBLEM 1.8

It is shown in textbooks of classical electrodynamics that an accelerated charge radiates energy at the rate

$$\frac{dE}{dt} = -\frac{2}{3}\frac{e^2a^2}{c^3} \tag{47}$$

where a is the acceleration, e the charge and c the velocity of light (Gaussian units are used here). Thus, an electron in an atom, according to the classical picture, will keep radiating energy and 'fall' into the nucleus. Estimate the time in which this would happen for a hydrogen atom, the electron initially executing a circular motion of radius 0.53×10^{-8} cm.

SOLUTIONS

SOLUTION 1.1

$$\frac{p^2}{2m} = E = 200 \text{ eV} = 3.2 \times 10^{-10} \text{ erg}$$

$$\therefore \qquad p = [2 \times 0.9 \times 10^{-27} \times 3.2 \times 10^{-10}]^{1/2} = 8 \times 10^{-19} \text{ gm cm/sec.}$$

Now

$$\Delta p_x \sim \frac{\hbar}{\Delta x} \simeq \frac{10^{-27} \text{ erg sec}}{2 \times 10^{-4} \text{ cm}} = 5 \times 10^{-24} \text{ gm cm/sec.}$$

$$\theta \sim \frac{\Delta p_x}{p} \approx 6 \times 10^{-6} \text{ radians} \simeq 1 \text{ sec of arc.}$$

SOLUTION 1.2

$$p \approx 10^2 \text{ cm gm/sec}, \quad \Delta p \approx \frac{\hbar}{\Delta x} \approx 5 \times 10^{-28} \text{ gm cm/sec.}$$

$$\theta \sim 5 \times 10^{-30} \text{ radians} \approx 10^{-24} \text{ sec of arc.}$$

SOLUTION 1.3

Let the dimensions of the region of localization for the first and second electrons be a_1 and a_2. Then the spread in momenta (and therefore the momenta themselves) would be given by

$$p_1 \sim \frac{\hbar}{a_1}, \quad p_2 \sim \frac{\hbar}{a_2} \tag{48}$$

Thus

$$\text{Kinetic energy} \sim \frac{\hbar^2}{2m}\left[\frac{1}{a_1^2} + \frac{1}{a_2^2}\right] \tag{49}$$

The potential energy of the interaction of the electrons with the nucleus with charge Ze is

$$-Ze^2\left(\frac{1}{a_1} + \frac{1}{a_2}\right)$$

and the interaction energy between the electrons is $\sim e^2/(a_1 + a_2)$ because the separation between the two electrons is $\sim (a_1 + a_2)$. The total energy is, therefore, given by

$$E\,(a_1, a_2) = \frac{\hbar^2}{2m}\left(\frac{1}{a_1^2} + \frac{1}{a_2^2}\right) - Ze^2\left(\frac{1}{a_1} + \frac{1}{a_2}\right) + \frac{e^2}{a_1 + a_2} \tag{50}$$

For E to be a minimum

$$0 = \frac{dE}{da_1} = -\frac{\hbar^2}{ma_1^3} + \frac{Ze^2}{a_1^2} - \frac{e^2}{(a_1 + a_2)^2}$$

$$0 = \frac{dE}{da_2} = -\frac{\hbar^2}{ma_2^3} + \frac{Ze^2}{a_2^2} - \frac{e^2}{(a_1 + a_2)^2}$$

The solution would be

$$a_1 = a_2 = \frac{\hbar^2}{me^2} \cdot \frac{1}{Z - 1/4} \tag{51}$$

$$\therefore \qquad E \simeq -(Z - 1/4)^2 \frac{me^4}{\hbar^2} = -(Z - 1/4)^2 \times 27.2 \text{ eV} \tag{52}$$

The values of E calculated using the above equation compare rather well with the experimental data as shown in Table 1.1. The energy is in units of $me^4/2\hbar^2 =$ 13.6 eV, the ionization potential of the hydrogen atom.

TABLE 1.1*

GROUND STATE ENERGY (IN UNITS OF $me^4/2\hbar^2$) OF VARIOUS TWO-ELECTRON ATOMS

	He	Li^+	Be^{++}	B^{+++}	C^{++++}
Experimental Value	-5.807	-14.56	-27.31	-44.06	-64.80
Calculated Value using Eq. (52)	-6.125	-15.12	-28.12	-45.12	-66.12

*After Goldman and Krivchenkov (1961).

SOLUTION 1.4

When a meson is emitted by one nucleon and absorbed by another, its position during transit is uncertain by an amount which is of the order of the range of the force. Thus

$$\Delta x \approx r_0$$

where r_0 is the range of the force. Using the uncertainty relation [Eq. (12)], we get

$$\Delta p \approx \frac{\hbar}{\Delta x} \approx \frac{\hbar}{r_0}$$

Further, for a relativistic particle

$$\Delta p \approx mc$$

$$\therefore \qquad mc \approx \frac{\hbar}{r_0}$$

or

$$r_0 \approx \frac{\hbar}{mc}$$

For $r_0 \approx 1.5 \times 10^{-13}$ cm, $m \approx 2 \times 10^{-25}$ gm $\approx 200\ m_e$, where m_e denotes the tron mass. This gives a rough estimate of the mass of the meson.

SOLUTION 1.5

The uncertainty in the particle mass Δm is

$$\Delta m \approx 2 \times 20\, m_e = 40\, m_e$$

where m_e is the electron mass.

Now $\quad E = mc^2$

$$\therefore \quad \Delta E = c^2\, \Delta m \approx 40\, m_e c^2$$

Now, from the uncertainty principle, the energy determination that has an accuracy ΔE must occupy at least a time interval Δt given by

$$\Delta t \simeq \frac{\hbar}{\Delta E} \simeq \frac{\hbar}{40\, m_e c^2} = \frac{1.05 \times 10^{-27} \text{ erg-sec}}{40 \times 0.9 \times 10^{-27} (\text{gm}) \times 9 \times 10^{20} (\text{cm/sec})^2}$$
$$\simeq 3 \times 10^{-23} \text{ sec}$$

Thus the mean life of the elementary particles observed in this experiment is about 3×10^{-23} sec.

SOLUTION 1.6

The proton is confined within a sphere of radius $r_0 \approx 10^{-13}$ cm. Thus the uncertainty in the momentum must be at least of the order of $\hbar/r_0$, or

$$p \simeq \frac{\hbar}{r_0}$$

Therefore, the kinetic energy of the proton will be given by

$$E = \frac{p^2}{2m_p} \sim \frac{\hbar^2}{2m_p r_0^2}$$

where m_p is the mass of the proton. On substitution, we get

$$E \sim \frac{(1.05 \times 10^{-27} \text{ erg-sec})^2}{2 \times 1.67 \times 10^{-24} \text{ g} \times (10^{-13} \text{ cm})^2}$$
$$\simeq 3 \times 10^{-5} \text{ ergs} \simeq 20 \text{ MeV}$$

Since the proton is bound inside the nucleus, the average of the potential energy, $\langle V \rangle$, must be negative and greater in magnitude than the kinetic energy. Therefore

$$-\langle V \rangle \gtrsim 20 \text{ MeV}$$

which indeed gives the correct order of the potential energy. The uncertainty in momentum for the electron is again $\hbar/r_0$ however, since the rest mass of the electron is very much smaller than that of the proton, the velocity of the electron is very close to c and we have to use the extreme relativistic formula for the energy,

$$E = cp = c\,\frac{\hbar}{r_0} = \frac{(3 \times 10^{10})\,(1.05 \times 10^{-27})}{10^{-13} \times 1.6 \times 10^{-6}} \text{ MeV} \sim 200 \text{ MeV}$$

Although electrons do emerge from nuclei in β-decay, they seldom have energies exceeding a few million electron volts. Thus one does not expect the electron to be a basic constituent of the nucleus; the rare occasions when β-decay occurs may be attributed to the transformation of a neutron into a proton and an electron (and the neutrino) so that the electron is in fact created at the instant the decay occurs.

SOLUTION 1.7

The energy of each photon will be

$$h\nu = \frac{hc}{\lambda} \simeq \frac{6.6 \times 10^{-34} \times 3 \times 10^{8}}{5 \times 10^{-7}} \simeq 4 \times 10^{-19}\ \text{J}.$$

Thus the number of photons emitted per second will be 2.5×10^{18} and the number of photons passing through hole S will approximately be

$$\frac{2.5 \times 10^{-18} \times \pi \times (0.02)^2}{4 \times \pi \times (100)^2} = 2.5 \times 10^{10} \text{ per second.}$$

The number of photons passing through either S_1 or S_2 will approximately be 10^3 per second and since it takes $\sim 3 \times 10^{-9}$ sec to traverse the distance between AB and the screen, one will almost never find two photons in the region between AB and the screen.

SOLUTION 1.8

The total energy $E = -(e^2/2r)$ where r is the radius. The acceleration is

$$a = \frac{v^2}{r} = \frac{e^2}{mr^2}$$

where v is the velocity, m the mass of the electron. The equation for the radiation rate may now be written as

$$\frac{dE}{dt} = \frac{e^2}{2r^2}\frac{dr}{dt} = -\frac{2}{3}\frac{e^2}{c^3}\left(\frac{e^2}{mr^2}\right)^2$$

an equation which can be readily integrated. The time t for the radius to collapse from r_0 to 0 is, then

$$t = \frac{r_0^3\, m^2c^3}{4e^4} \approx 1.6 \times 10^{-11} \text{ sec.}$$

CHAPTER TWO

Time Dependent Schrodinger Equation and Wave Packets

2.1 Introduction

In the previous chapter we discussed some expriments which showed that particles like electrons, protons, neutrons, atoms, etc. exhibit wave like properties. Indeed the wavelength is related to the momentum through the de Broglie relation

$$\lambda = \frac{h}{p} \tag{1}$$

or

$$p = \hbar k \tag{2}$$

where $k = 2\pi/\lambda$. Thus we may write

$$\mathbf{p} = \hbar \mathbf{k} \tag{3}$$

where $\mathbf{k}$ denotes the wave vector. Further, as established by Einstein's explanation of the photoelectric effect, the energy E of the particle is related to the frequency through the relation

$$E = \hbar\omega \tag{4}$$

In this chapter we would like to obtain an equation the solution of which would describe the behaviour of a particle like electron, proton*, etc. The corresponding solutions should describe the corpuscular and wavelike behaviour of the particle and should also be consistent with the uncertainty principle. Thus we assume that the trajectory of a particle should be describable by a wave function $\Psi(\mathbf{r}, t)$ whose magnitude is large in regions where the probability of the occurrence of the particle is large; in other regions where the particle is less likely to be found, the magnitude of Ψ should be small. Indeed we will show that $|\Psi|^2\, d\tau$ can be interpreted to represent the probability of finding the particle in the volume element $d\tau$.

In Sec. 2.2 we will obtain an equation (known as the Schrödinger equation) satisfied by Ψ and will show that in quantum mechanics the dynamical variables like position, momentum, energy, etc. are to be considered as operators which will lead to the commutation relation as discussed in Sec. 2.3. In Sec. 2.4 we will give a physical interpretation of the wavefunction and in Sec. 2.5 we will give formulae which will enable us to calculate the expectation values of various observables (like position, momentum, energy, etc.) if the particle is described by the wave function Ψ; such considerations will immediately lead to the relation between classical and quantum motions (Ehrenfest's theorem) and also to the uncertainty principle which will be quantitatively discussed in Sec. 2.6. In Sec. 2.7 we will discuss the motion of a wave packet which will describe the trajectory of a free particle; the wave function describing the motion of the wave packet will obviously be a solution of the Schrödinger equation and will be shown to be consistent with the uncertainty principle. Finally in Sec. 2.8 we will discuss the propagation of a Gaussian wave packet. In Chapters 3, 4 and 5 we will obtain exact solutions of the Schrödinger equation corresponding to problems of physical interest.

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*As discussed in Chapter 1, radiation also exhibits wave and particle like properties. The quantum theory of radiation is discussed in Chapter 22.

2.2 The Schrödinger Equation

The simplest type of a wave is a plane monochromatic wave described by the wave function

$$\Psi(\mathbf{r}, t) = A e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \tag{5}$$

which represents a disturbance of amplitude A and of wavelength $\lambda = 2\pi/k$ travelling in the direction of its wave vector $\mathbf{k}$ with phase velocity ω/k. If we assume the propagation to be along the x-axis then

$$\mathbf{k} = k\mathbf{x} \tag{6}$$

and we have

$$\Psi(x, t) = A e^{i(kx - \omega t)} \tag{7}$$

which on using Eqs. (2) and (4) takes the form

$$\Psi(x, t) = A \exp\left[\frac{i}{\hbar}\left(px - Et\right)\right] \tag{8}$$

Successive differentiation of Eq. (8) gives us

$$i\hbar \frac{\partial \Psi}{\partial t} = E\Psi(x, t) \tag{9}$$

$$-i\hbar \frac{\partial \Psi}{\partial x} = p\Psi(x, t) \tag{10}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m}\Psi(x, t) \tag{11}$$

Now for a free non-relativistic particle

$$E = \frac{p^2}{2m} \tag{12}$$

and therefore

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} \tag{13}$$

which is the one dimensional time dependent Schrödinger equation* for a free particle. Further, Eqs. (9) and (10) suggest that E and p can be represented by the operators $i\hbar\,\partial/\partial t$ and $-i\hbar\,\partial/\partial x$ respectively:

$$E \rightarrow i\hbar \frac{\partial}{\partial t}, \quad p \rightarrow -i\hbar \frac{\partial}{\partial x} \tag{14}$$

Thus Eq. (13) can also be written in the form

$$E\Psi = \frac{p^2}{2m}\Psi(x, t) \tag{15}$$

where it is implied that E and p are to be replaced by their operator representations.

The three dimensional generalization is very straightforward. Instead of Eq. (8) we have

$$\begin{aligned}\Psi(\mathbf{r}, t) &= A \exp\left[\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r} - Et\right)\right] \\ &= A \exp\left[\frac{i}{\hbar}\left(p_x x + p_y y + p_z z - Et\right)\right]\end{aligned} \tag{16}$$

Thus

$$i\hbar \frac{\partial\Psi}{\partial t} = E\Psi$$

$$-i\hbar \frac{\partial\Psi}{\partial x} = p_x\Psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{p_x^2}{2m}\Psi$$

etc. Since

$$E = \frac{p^2}{2m} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \tag{17}$$

we immediately have

$$i\hbar \frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right] = -\frac{\hbar^2}{2m}\nabla^2\Psi \tag{18}$$

---

*By using the method of separation of variables, one can easily show that the general solution of Eq. (13) can be written in the form (see Problem 2.1)

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} a(p) \exp\left[\frac{i}{\hbar}\left(px - Et\right)\right] dp$$

with $E = p^2/2m$. The above equation describes a wave packet which is nothing but superposition of plane waves. We will study the propagation of such a wave packet in Secs. 2.7 and 2.8.

which is the 3-dimensional Schrödinger equation for a free particle. Once again the operator representation of E and components of $\mathbf{p}$ would be

$$E \to i\hbar\,\frac{\partial}{\partial t};\quad \mathbf{p} \to -i\hbar\,\nabla \tag{19}$$

where the last step implies[*] $p_x \to -i\hbar\,\partial/\partial x$, $p_y \to -i\hbar\,\partial/\partial y$ and $p_z \to -i\hbar\,\partial/\partial z$. Further, Eq. (18) can be written in the form

$$E\Psi = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)\Psi = \frac{p^2}{2m}\Psi \tag{20}$$

Till now we have assumed the particle to be free. If we now assume the particle to be in a field characterised by the potential energy function $V(\mathbf{r}, t)$ then according to classical mechanics the total energy would be given by

$$E = \frac{p^2}{2m} + V(\mathbf{r}, t) \tag{21}$$

Since the potential energy function does not depend on p and E, Eqs. (19), (20) and (21) suggest that the wave function should satisfy

$$i\hbar\,\frac{\partial\Psi}{\partial t} = \left[\frac{p^2}{2m} + V(\mathbf{r}, t)\right]\Psi = \left[-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi\right] \tag{22}$$

which is the time dependent Schrödinger equation for a particle in a field characterised by the potential energy function $V(\mathbf{r}, t)$. Equation (22) is usually written in the form

$$i\hbar\,\frac{\partial\Psi}{\partial t} = H\Psi \tag{23}$$

where

$$H = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\nabla^2 + V \tag{24}$$

is known as the Hamiltonian operator. The corresponding one dimensional

---

[*] At this point it is necessary to mention that the entire theory could have been equally well developed if we had assumed

$$\Psi = \exp\left[-\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r} - Et\right)\right]$$

to represent a plane wave propagating in the direction of $\mathbf{p}$. The operator representations of E and p would then have been $E \to -i\hbar\,\partial/\partial t$ and $\mathbf{p} \to +i\hbar\,\nabla$ and the Schrödinger equation for a free particle would have been (cf. Eq. 18)

$$-i\hbar\,\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi$$

The later analysis and the various solutions could have been obtained in a similar manner. However the sine and cosine functions of the type $\sin\,(px - Et)/\hbar$—which also represent plane waves—are quite unsuitable because then the operator representation of the type given by Eq. (19) would not have been possible.

equation is

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right]\Psi \tag{25}$$

It should be mentioned that the method for obtaining the Schrödinger equation is far from being rigorous. We have tried to fit together the corpuscular and wave characteristics of the particle and have assumed that the particle can be described by a wave function Ψ which, in general, is complex and satisfies Eq. (22). By solving Eq. (22) (under appropriate boundary and initial conditions) one can predict the results of various measurements which we will do in this and the following chapters. Indeed the validity of the Schrödinger equation comes from the agreement of the theoretical results (obtained by solving the Schrödinger equation) with experimental data.

2.3 The Commutator

Because of the operator representation of p_x (see Eq. 19) we have

$$[xp_x - p_x x]\,\Psi = -i\hbar\left[x\frac{\partial\Psi}{\partial x} - \frac{\partial}{\partial x}(x\Psi)\right]$$

or

$$[xp_x - p_x x]\,\Psi = i\hbar\Psi$$

Since Ψ is an arbitrary function, the operator $[xp_x - p_x x]/i\hbar$ is simply an unit operator. We write

$$[xp_x - p_x x] \equiv [x, p_x] = i\hbar \tag{26}$$

which is known as the commutation relation. The quantity

$$[\alpha, \beta] = \alpha\beta - \beta\alpha = -[\beta, \alpha] \tag{27}$$

is said to be the commutator of the two operators α and β. It is easy to show that

$$[x, y] = [x, z] = 0$$
$$[x, p_y] = [y, p_z] = 0$$
$$[p_x, p_y] = [p_x, p_z] = 0$$

But

$$[y, p_y] = [z, p_z] = i\hbar$$

Commutation relations play a very important role in quantum mechanics and we will use them in later chapters (see e.g., Chapters 8, 9, etc.).

2.4 Physical Interpretation of Ψ and the Probability Current Density

We rewrite the Schrödinger equation (Eq. 22)

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \tag{28}$$

and its complex conjugate

$$-i\hbar\frac{\partial\Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^* \tag{29}$$

where $V(\mathbf{r}, t)$ is assumed to be real. If we multiply Eq. (28) by Ψ^* and Eq. (29) by Ψ and subtract we would obtain

$$i\hbar\left[\Psi^*\frac{\partial\Psi}{\partial t}+\Psi\frac{\partial\Psi^*}{\partial t}\right] = -\frac{\hbar^2}{2m}\left[\Psi^*\nabla^2\Psi-\Psi\nabla^2\Psi^*\right] \tag{30}$$

Since $\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$, we can rewrite the above equation in the form

$$\frac{\partial}{\partial t}(\Psi^*\Psi)+\left[\frac{\partial J_x}{\partial x}+\frac{\partial J_y}{\partial y}+\frac{\partial J_z}{\partial z}\right]=0 \tag{31}$$

where

$$J_x = \frac{i\hbar}{2m}\left[\Psi\frac{\partial\Psi^*}{\partial x}-\Psi^*\frac{\partial\Psi}{\partial x}\right]$$

$$J_y = \frac{i\hbar}{2m}\left[\Psi\frac{\partial\Psi^*}{\partial y}-\Psi^*\frac{\partial\Psi}{\partial y}\right]$$

$$J_z = \frac{i\hbar}{2m}\left[\Psi\frac{\partial\Psi^*}{\partial z}-\Psi^*\frac{\partial\Psi}{\partial z}\right]$$

Equation (31) can be written in the form*

$$\frac{\partial\rho}{\partial t}+\nabla\cdot\mathbf{J}=0 \tag{32}$$

where

$$\rho = \Psi^*\Psi \tag{33}$$

and

$$\mathbf{J} = \frac{i\hbar}{2m}\left[\Psi\nabla\Psi^*-\Psi^*\nabla\Psi\right] \tag{34}$$

Equation (32) is nothing but the equation of continuity in fluid dynamics (see Appendix C) where ρ represents the number of particles per unit volume and **J** the current density. Thus we may associate $\Psi^*\Psi$ with *position probability density* in the sense that $\Psi^*\Psi\, d\tau$ will be proportional to the probability of finding the particle in volume element $d\tau$. Now, since the Schrödinger equation is a linear equation, a multiple of Ψ would also be a solution and we may choose the multiplicative constant such that

$$\iiint|\Psi|^2\, d\tau = 1 \tag{35}$$

---

*Equation (32) could have been directly written by using vector algebra as

$$\frac{i\hbar}{2m}\left[\Psi^*\nabla^2\Psi-\Psi\nabla^2\Psi^*\right]=\frac{i\hbar}{2m}\nabla\cdot\left[\Psi^*\nabla\Psi-\Psi\nabla\Psi^*\right]$$
$$=\nabla\cdot\mathbf{J}$$

where the integration is over the entire space. Equation (35) is known as the normalization condition. If the wave function is normalized (i.e., if it satisfies Eq. 35) then $|\Psi|^2 d\tau$ can be interpreted to represent the probability of finding the particle in the volume element $d\tau$ and Eq. (35) implies the fact that the particle has to be found somewhere in space. Further,

$$\mathbf{J} = \frac{i\hbar}{2m}\left[\Psi\nabla\Psi^* - \Psi^*\nabla\Psi\right] = \text{Re}\left[\Psi^*\frac{\hbar}{im}\nabla\Psi\right] \tag{36}$$

can be associated with *probability current density* (see Appendix C). Here Re stands for the real part of the quantity inside the bracket. It is of interest to mention that the quantity $-i\hbar\nabla$ represents the momentum operator $\mathbf{p}$ (see Eq. 19) and therefore we may write

$$\mathbf{J} = \text{Re}\,[\Psi^*\mathbf{v}\Psi] \tag{37}$$

where $\mathbf{v} = \mathbf{p}/m$ represents the velocity operator. Equations (33) and (37) are consistent with the fact that in fluid dynamics

$$\mathbf{J} = \rho\mathbf{v} \tag{38}$$

As an example we consider the wave function

$$\Psi = \exp\left[\frac{i}{\hbar}\left(\mathbf{p}\cdot\mathbf{r} - Et\right)\right] \tag{39}$$

which, however, cannot be normalized as the position probability density is constant everywhere.* But

$$\mathbf{J} = \text{Re}\left[\Psi^*\frac{\hbar}{im}\nabla\Psi\right] = \frac{\mathbf{p}}{m} = \mathbf{v} \tag{40}$$

which is consistent with Eq. (38) because $\rho = 1$. It may be noted that in Eqs. (39) and (40), $\mathbf{p}$ and E are numbers.

We conclude this section by noting that

$$\begin{aligned}\frac{\partial}{\partial t}\int_\Omega \Psi^*\Psi d\tau &= \int_\Omega \frac{\partial\rho}{\partial t}\,d\tau = -\int_\Omega \nabla\cdot\mathbf{J}\,d\tau \\ &= -\int_S \mathbf{J}\cdot\hat{\mathbf{n}}\,dS \end{aligned} \tag{41}$$

where Ω represents an arbitrary volume bounded by the surface S and in the last step we have used Gauss's theorem. Thus if the integration is carried over the entire space and if the wave function vanishes at infinity then

$$\frac{\partial}{\partial t}\iiint|\Psi|^2\,d\tau = 0 \tag{42}$$

which is essentially the conservation condition.

---

*A realistic wave function will be a wave packet, see, e.g. Problem 2.3.

2.5 Expectation Values

By associating $\Psi^*\Psi$ with position probability density we can calculate the expectation or average values of the position of the particle. Thus the expectation value of the x-coordinate would be given by

$$\langle x \rangle = \frac{\iiint x\Psi^*\Psi d\tau}{\iiint \Psi^*\Psi d\tau} \tag{43}$$

where the integration is over the entire space. If we assume the wave function to be normalized [see Eq. (35)] then

$$\langle x \rangle = \int \Psi^* x \Psi d\tau \tag{44}$$

where for the sake of convenience we are replacing the triple integral sign by a single integral. We have also put x between Ψ^* and Ψ for reasons which will become clear later in this section. In a similar manner we can write for $\langle y \rangle$ and $\langle z \rangle$. In general, for any function $f(\mathbf{r})$, the expectation value will be given by

$$\langle f(\mathbf{r}) \rangle = \int \Psi^* f(\mathbf{r}) \Psi d\tau \tag{45}$$

In particular

$$\langle V(\mathbf{r}, t) \rangle = \int \Psi^* V(\mathbf{r}, t) \Psi d\tau \tag{46}$$

Now since $E = p^2/2m + V$, we should have

$$\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V \rangle \tag{47}$$

Further, if we multiply the Schrödinger equation [Eq. (22)] by Ψ^* and integrate over all space we would get

$$\int \Psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \Psi d\tau = \int \Psi^* \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \Psi d\tau + \int \Psi^* V(\mathbf{r}, t) \Psi d\tau \tag{48}$$

The last term in this equation is simply $\langle V \rangle$ [see Eq. (46)] and therefore Eqs. (46), (47) and (48) will be consistent only if we assume

$$\langle E \rangle = \int \Psi^* i\hbar \frac{\partial}{\partial t} \Psi d\tau \tag{49}$$

and

$$\left\langle \frac{p^2}{2m} \right\rangle = \int \Psi^* \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \Psi d\tau \tag{50}$$

Since $i\hbar\, \partial/\partial t$ and $-(\hbar^2/2m)\, \nabla^2$ are the operator representations of E and $p^2/2m$ we can say that the general recipe of determining the expectation value of any quantity is to replace it by its operator representation, operate it on Ψ and preply by Ψ^* and then integrate. Thus

$$\langle p_x \rangle = \int \Psi^* \left(-i\hbar \frac{\partial \Psi}{\partial x} \right) d\tau \tag{51}$$

$$\langle p_x^2 \rangle = \int \Psi^* \left(-\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \right) d\tau \tag{52}$$

$$\langle p_y \rangle = \int \Psi^* \left(-i\hbar \frac{\partial \Psi}{\partial y} \right) d\tau \tag{53}$$

etc. Using the above recipe for calculation of the expectation values and also using the Schrödinger equation one can show that (see Problem 2.9)

$$\frac{d}{dt} \langle x \rangle = \frac{1}{m} \langle p_x \rangle \tag{54}$$

$$\frac{d}{dt} \langle p_x \rangle = - \left\langle \frac{\partial V}{\partial x} \right\rangle \tag{55}$$

The above equations show that there is agreement between quantum and classical motions in the sense that in quantum theory the expectation values satisfy the Newton's laws of motion. Equations (54) and (55) were first derived by Ehrenfest and the general relationship (between classical and quantum motions) is known as Ehrenfest's theorem.

In the next section we will use the various expressions for the expectation values to give an exact statement of the uncertainty principle.

2.6 Exact Statement and Proof of the Uncertainty Principle

In Chapter 1 we had discussed experiments which showed that it is not possible to measure simultaneously the position of a particle along a particular (say x) direction and also the corresponding momentum p_x with unlimited accuracy. Indeed we showed that $\Delta x \Delta p_x \gtrsim h$, where Δx and Δp_x were uncertainties in the measurement of x and p_x respectively. In this section we will give precise definitions of Δx and Δp_x and using the results of previous sections, we will make an exact statement of the uncertainty principle. First, in analogy with the definition of standard deviation in statistics, we define the uncertainties in x and p_x as

$$\Delta x = \langle (x - \langle x \rangle)^2 \rangle^{1/2} = [\langle x^2 \rangle - \langle x \rangle^2]^{1/2} \tag{56}$$

$$\Delta p = \langle (p - \langle p \rangle)^2 \rangle^{1/2} = [\langle p^2 \rangle - \langle p \rangle^2]^{1/2} \tag{57}$$

where, for the sake of convenience, we have dropped the subscript on p. We will establish that

$$\Delta x \, \Delta p \geqslant \frac{1}{2} \hbar \tag{58}$$

which is the exact statement of the uncertainty principle. In order to prove Eq. (58) we would require the following inequality

$$\int f^* f d\tau \int g^* g d\tau \geqslant \frac{1}{4} \left[\int \left(f^* g + f g^* \right) d\tau \right]^2 \tag{59}$$

where f and g are arbitrary functions of the space coordinates; however, they must be single valued and all the integrals in Eq. (59) must exist. The proof of Eq. (59) is quite simple. We define three integrals

$$a = \int f^* f d\tau, \quad b = \int f^* g d\tau, \quad c = \int g^* g d\tau$$

Now

$$\int |\lambda f + g|^2 \, d\tau = a\lambda^2 + (b + b^*)\lambda + c \geqslant 0$$

Because $|\lambda f + g|^2 \geqslant 0$ everywhere and we are assuming λ to be a real quantity. Obviously for the above inequality to be satisfied we must have

$$4ac \geqslant (b + b^*)^2$$

which proves Eq. (59); the equality sign will occur when f is a multiple of g.

We will consider the special case* of $\langle x \rangle = 0$ and $\langle p \rangle = 0$ and assume

$$f = p\Psi = -i\hbar \frac{\partial \Psi}{\partial x} \tag{60}$$

$$g = ix\Psi \tag{61}$$

Thus

$$\begin{aligned} \int f^* f d\tau &= \hbar^2 \iint dy\, dz \int \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} dx \\ &= \hbar^2 \iint dy\, dz \left[\Psi^* \frac{\partial \Psi}{\partial x} \Big|_{-\infty}^{+\infty} - \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2} dx \right] \\ &= \iiint \Psi^* \left(-\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \right) dx\, dy\, dz = \langle p^2 \rangle \end{aligned}$$

where we have used Eq. (52) and the fact that Ψ vanishes at infinity. Further,

$$\int g^* g d\tau = \int \Psi^* x^2 \Psi d\tau = \langle x^2 \rangle$$

and

$$\begin{aligned} \int \left(f^* g + f g^* \right) d\tau &= -\hbar \int \frac{\partial \Psi^*}{\partial x} x \Psi d\tau - \hbar \int \frac{\partial \Psi}{\partial x} x \Psi^* d\tau \\ &= -\hbar \int \frac{\partial}{\partial x} \left(\Psi^* x \Psi \right) d\tau + \hbar \int \Psi^* \Psi d\tau \\ &= \hbar \end{aligned}$$

because Ψ is normalized and $\Psi^* x \Psi$ would vanish at $x = \pm\infty$. On substitution in Eq. (59), we immediately get the uncertainty relation given by Eq. (58).

---

*For $\langle x \rangle \neq 0$ and $\langle p \rangle \neq 0$, we must choose

$$f = (p - \langle p \rangle)\Psi$$

and

$$g = (x - \langle x \rangle)\Psi$$

The uncertainty product is a minimum for a Gaussian wave function (see Problem 2.20).

2.7 The One Dimensional Wave Packet: Concept of Group and Phase Velocities

In order to describe the corpuscular properties of a free particle, we describe it by a wave packet obtained by the superposition of plane waves

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} A(k) e^{i(kx-\omega t)}\, dk \tag{62}$$

where, for the sake of simplicity, we are restricting our considerations to one dimensional motion only; the three dimensional generalization is quite straightforward (see Problems 2.19 and 2.21). Now using Eqs. (2) and (4) we may write Eq. (62) in the form

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} a(p) \exp\left[\frac{i}{\hbar}\left(px - Et\right)\right] dp \tag{63}$$

Thus

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} a(p) \exp\left[\frac{i}{\hbar} px\right] dp \tag{64}$$

where the factor $1/(2\pi\hbar)^{1/2}$ has been introduced so that (by using Fourier theorem—see Appendix D) $a(p)$ is given by the symmetrical relation

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x, 0) \exp\left[-\frac{i}{\hbar} px\right] dx \tag{65}$$

Since, for a free non-relativistic particle

$$E = p^2/2m \tag{66}$$

Eq. (62) is the most general solution of the one dimensional Schrödinger equation (see Problem 2.1).

If Ψ is normalised, it is easy to show that (see Problem 2.7)

$$\int \left| a(p) \right|^2 dp = 1 \tag{67}$$

$$\langle p \rangle = \int_{-\infty}^{+\infty} p \, | a(p) |^2 \, dp \tag{68}$$

$$\langle p^2 \rangle = \int_{-\infty}^{+\infty} p^2 \, | a(p) |^2 \, dp \tag{69}$$

etc. which show that $|a(p)|^2\,dp$ can be interpreted as the probability of the x-component of the momentum to lie between p and $p + dp$.

Equation (66) along with Eqs. (2) and (4) gives us

$$\omega = \frac{\hbar}{2m} k^2 \tag{70}$$

which is the $\omega - k$ relation or the dispersion relation* for matter waves in free space.

We will next show that if there exists a small range of k values for which the amplitudes of the component waves have significant values then it is possible to assign an average velocity to the wave packet. This average velocity is known as the group velocity. We write

$$A(k) = |A(k)|\, e^{i\phi(k)} \tag{71}$$

and assume that $|A(k)|$ is very sharply peaked when k lies in a small interval Δk around $k = k_0$ and negligible everywhere else so that we may write

$$\Psi(x, t) \approx \frac{1}{\sqrt{2\pi}} \int_{\Delta k} |A(k)|\, e^{i[kx - \omega(k)t + \phi(k)]}\, dk \tag{72}$$

where the integration extends over the domain Δk where $|A(k)|$ has appreciable values. Next, we make Taylor expansions of $\omega(k)$ and $\phi(k)$ around $k = k_0$ and get

$$\omega(k) = \omega(k_0) + \left.\frac{d\omega}{dk}\right|_{k=k_0}(k - k_0) + \tfrac{1}{2}\left.\frac{d^2\omega}{dk^2}\right|_{k=k_0}(k - k_0)^2 + \ldots \tag{73}$$

$$\phi(k) = \phi(k_0) + \left.\frac{d\phi}{dk}\right|_{k=k_0}(k - k_0) + \tfrac{1}{2}\left.\frac{d^2\phi}{dk^2}\right|_{k=k_0}(k - k_0)^2 + \ldots \tag{74}$$

We substitute the above expansions in Eq. (72) and assume that in the domain of integration Δk, $\omega(k)$ and $\phi(k)$ do not vary significantly so that the terms involving quadratic and higher powers of $(k - k_0)$ can be neglected; under such an approximation, we get

$$\Psi(x, t) \approx f(x, t)\, e^{i(k_0 x - \omega_0 t + \phi_0)} \tag{75}$$

---

*A medium is said to be non-dispersive when the $\omega - k$ relation is linear. For example, for electromagnetic waves in free space

$$\omega(k) = ck$$

where c represents the speed of light in free space. For such a case, Eq. (62) becomes

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} A(k)\, e^{ik(x - ct)} dk$$

$$= f(x - ct)$$

implying that the packet travels undistorted with speed c. Thus free space is a non-dispersive medium for electromagnetic waves. On the other hand, whenever the $\omega - k$ relationship is not linear (see, e.g., Eq. 70) the medium is said to be dispersive and a wave packet undergoes distortion (see Sec. 2.8).

where $\omega_0 \equiv \omega(k_0)$, $\phi_0 \equiv \phi(k_0)$ and $f(x, t)$, which represents the envelope of the wave packet, is given by

$$f(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\Delta k} |A(k)|\, e^{i(k-k_0)(x-x_0-v_g t)} dk \tag{76}$$

where

$$x_0 = -\left.\frac{d\phi}{dk}\right|_{k=k_0} \quad \text{and} \quad v_g = \left.\frac{d\omega}{dk}\right|_{k=k_0} \tag{77}$$

Since the function $f(x, t)$ depends on x and t only through the combination $x - v_g t$, the wave packet propagates without any distortion with velocity v_g which is known as the group velocity of the packet. It should be pointed out that the packet remains undistorted as long as the neglect of second and higher order terms in Eqs. (73) and (74) are justified (see Problem 2.16 and Sec. 2.8). However, if the $\omega - k$ relation is strictly linear, the packet will never undergo any distortion (see footnote on page 62).

Now, from Eq. (76) we have

$$f(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{\Delta k} |A(k)|\, e^{i(k-k_0)(x-x_0)} dk \tag{78}$$

It is immediately seen that at $x = x_0$, the integrand is everywhere positive and the value of the integral is maximum. For $|x - x_0| \gtrsim 1/\Delta k$ the exponential function oscillates rapidly in the domain of integration and the value of the integral is very small. This immediately leads to the relation

$$\Delta k\, \Delta x \gtrsim 1 \tag{79}$$

which when multiplied by $\hbar$ gives the uncertainty relation.

Thus, at $t = 0$ the wave packet is sharply peaked at $x = x_0$ and as t increases the centre of the packet, $x_c(t)$, moves according to the equation

$$x_c(t) = x_0 + v_g t \tag{80}$$

This will be explicitly seen in the next section when we consider the spreading of a Gaussian wave packet.

Now using Eqs. (2) and (4), we get

$$v_g = \frac{d\omega}{dk} = \frac{dE}{dp} \tag{81}$$

Thus for a non-relativistic particle for which $E = p^2/2m$, we have

$$v_g = \frac{dE}{dp} = \frac{p}{m} = v \tag{82}$$

Further, for a relativistic particle

$$E^2 = p^2c^2 + m^2c^4$$

and we have

$$\frac{dE}{dp} = \frac{pc^2}{E}$$

But

$$E = \frac{mc^2}{\sqrt{1 - v^2/c^2}} \quad \text{and} \quad p = \frac{mv}{\sqrt{1 - v^2/c^2}}$$

giving

$$pc^2/E = v$$

Thus

$$v_g = v \tag{83}$$

Equations (82) and (83) tell us that the group velocity of the packet is to be associated with the velocity of the particle.

The phase velocity v_p is defined through the relation

$$v_p = \omega/k \tag{84}$$

and represents the velocity of propagation of an infinitely long monochromatic plane wave. Only when ω is proportional to k, v_p and v_g are equal. In general, it is the group velocity of a packet which is of physical significance.

2.8 The One Dimensional Gaussian Wave Packet*

As an example, we consider the propagation of a Gaussian wave packet for which

$$\Psi(x, t = 0) = \frac{1}{(\pi\sigma^2)^{1/4}} \exp\left[-\frac{(x - x_0)^2}{2\sigma^2}\right] \exp\left[\frac{i}{\hbar} p_0 x\right] \tag{85}$$

The wave function is normalized and if we plot $|\Psi|^2$ as a function of x we will find that it is peaked around $x = x_0$ and that the particle is most likely to be found in the region $\Delta x \sim \sigma$. Indeed from rigorous calculations

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^* x \Psi \, dx = x_0, \quad \langle x^2 \rangle = \frac{\sigma^2}{2} + x_0^2 \tag{86}$$

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^* \left(-i\hbar \frac{\partial \Psi}{\partial x}\right) dx = p_0, \quad \langle p^2 \rangle = \frac{\hbar^2}{2\sigma^2} + p_0^2 \tag{87}$$

so that

$$\Delta x = \left[\langle x^2 \rangle - \langle x \rangle^2\right]^{\frac{1}{2}} = \frac{\sigma}{\sqrt{2}} \tag{88}$$

and

$$\Delta p = \left[\langle p^2 \rangle - \langle p \rangle^2\right]^{\frac{1}{2}} = \frac{\hbar}{\sigma\sqrt{2}} \tag{89}$$

Thus

$$\Delta x \, \Delta p = \tfrac{1}{2}\hbar \tag{90}$$

consistent with the uncertainty principle. If we substitute for $\Psi(x, 0)$ in Eq. (65)

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*The three dimensional Gaussian wave packet is discussed in the solution of Problem 2.19.

and carry out the integration we would get

$$a(p) = \left(\frac{\sigma^2}{\pi\hbar^2}\right)^{\frac{1}{4}} \exp\left[-\frac{\sigma^2}{2\hbar^2}\left(p - p_0\right)^2 - \frac{i}{\hbar}\left(p - p_0\right)x_0\right] \tag{91}$$

where use has to be made of the integral (see Appendix E)

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} e^{-\beta x} dx = \left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}} \exp\left(\beta^2/4\alpha\right) \tag{92}$$

Thus $|a(p)|^2$ is peaked at $p = p_0$ with $\Delta p \sim \hbar/\sigma$ consistent with Eq. (89) (see also Problem 2.12). Now,

$$\Psi(x, t) = \frac{1}{(2\pi\hbar)^{1/2}} \int a(p) \exp\left[\frac{i}{\hbar}\left(px - \frac{p^2}{2m}t\right)\right] dp$$
$$= \left(\frac{\sigma^2}{\pi\hbar^2}\right)^{1/4} \frac{1}{(2\pi\hbar)^{1/2}} e^{\gamma} \int e^{-\alpha p^2} e^{\beta p} \, dp$$

where

$$\alpha = \frac{\sigma^2}{2\hbar^2} + \frac{it}{2m\hbar}, \quad \beta = \frac{\sigma^2}{\hbar^2} p_0 + \frac{i}{\hbar}(x - x_0)$$

and

$$\gamma = -\frac{\sigma^2 p_0^2}{2\hbar^2} + \frac{i}{\hbar} p_0 x_0$$

On using Eq. (92) we get

$$|\Psi(x, t)|^2 = \frac{1}{[\pi\sigma_1^2(t)]^{1/2}} \exp\left[-\frac{\left\{x - \left(x_0 + \frac{p_0}{m}t\right)\right\}^2}{\sigma_1^2(t)}\right] \tag{93}$$

where

$${}_1(t) = \sigma\left[1 + \frac{\hbar^2 t^2}{m^2\sigma^4}\right]^{1/2} \tag{94}$$

Thus the centre of the packet moves with the velocity p_0/m consistent with the expression for group velocity

$$v_g = \left.\frac{d\omega}{dk}\right|_{k=k_0} = \left.\frac{dE}{dp}\right|_{p=p_0} = \frac{1}{m} p_0 \tag{95}$$

Further, $\phi(k)$ [see Eqs. (71) and (91)] is given by

$$\phi(k) = -\frac{1}{\hbar}(p - p_0)\,x_0 = -(k - k_0)\,x_0 \tag{96}$$

Thus the centre of the wave packet $\left(= -\left.\frac{d\psi}{dk}\right|_{k=k_0}\right)$ is x_0 at $t = 0$ consistent with Eq. (80). Finally we note that since the medium is dispersive the width of the packet [$\sim \sigma_1(t)$] increases with time (see Fig. 2.1). Indeed

$$\Delta x = \frac{\sigma}{\sqrt{2}}\left[1 + \frac{\hbar^2 t^2}{\sigma^4 m^2}\right]^{1/2} \quad \text{and} \quad \Delta p = \frac{\hbar}{\sigma\sqrt{2}} \tag{97}$$

so that

$$\Delta x\,\Delta p = \frac{1}{2}\hbar\left[\frac{1 + \hbar^2 t^2}{\sigma^4 m^2}\right]^{\frac{1}{2}} \tag{98}$$

The time in which there is considerable distortion of the wave packet is given by

$$t_0 \approx \frac{\sigma^2 m}{\hbar} \approx \frac{2m\,(\Delta x)^2}{\hbar} \tag{99}$$

consistent with the findings of Problem 2.16.

PROBLEMS

PROBLEM 2.1

Using the method of separation of variables show that the general solution of the one dimensional Schrödinger equation for a free particle [Eq. (13)] is given by

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}}\int a(p)\exp\left[\frac{i}{\hbar}\left(px - \frac{p^2}{2m}\right)t\right]dp \tag{100}$$

PROBLEM 2.2

Using the operator representations of p_x, p_y and p_z prove that

$$\begin{aligned} [x,\ p_y] &= 0 = [y, p_z] \\ [p_x, p_y] &= 0 = [p_x, p_z] \\ [y,\ p_y] &= i\hbar = [z, p_z] \end{aligned} \tag{101}$$

PROBLEM 2.3

For the Gaussian wave packet given by Eq. (85) show that

$$\mathbf{J} = \frac{1}{(\pi\sigma^2)^{1/2}}\exp\left[-\frac{(x - x_0)^2}{2\sigma^2}\right]\frac{p_0}{m}\,\hat{\mathbf{x}} \tag{102}$$

and interpret the result physically.

PROBLEM 2.4

Calculate $\mathbf{J}$ for $\Psi = 1/r \exp(ikr)$, $r = (x^2 + y^2 + z^2)^{1/2}$ and interpret the result physically.

PROBLEM 2.5

Show by partial integration of Eq. (51) that $\langle p_x \rangle$ is real.

PROBLEM 2.6

For a one dimensional wave packet show that

$$\int J\,dx = \frac{\langle p \rangle}{m} \tag{103}$$

Discuss the physical significance and generalize to three dimensions.

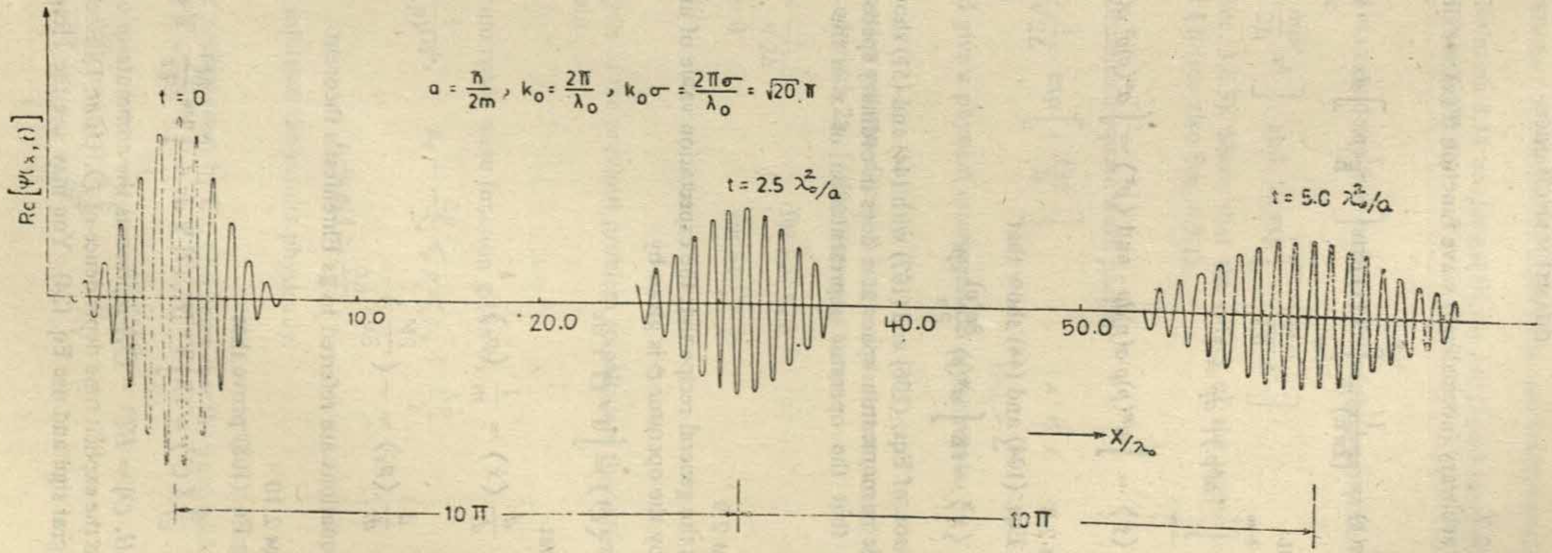

Fig. 2.1 The propagation and broadening of a Gaussian wave packet.

PROBLEM 2.7

For an arbitrary (normalized) wave function $\Psi(x)$, we define

$$a(p) = \frac{1}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{+\infty} \Psi(x) \exp\left[-\frac{i}{\hbar} px\right] dx \tag{104}$$

Show that

$$\int_{-\infty}^{+\infty} |a(p)|^2 \, dp = 1 \tag{105}$$

$$\langle p \rangle = \int a^*(p) p \, a(p) dp \quad \text{and} \quad \langle p^2 \rangle = \int a^*(p) p^2 \, a(p) dp \tag{106}$$

PROBLEM 2.8

Using Eqs. (104) and (44) show that

$$\langle x \rangle = i\hbar \int a^*(p) \frac{\partial a(p)}{\partial p} dp \tag{107}$$

Comparison of Eqs. (106) and (107) with (44) and (51) show that $a(p)$ plays the same role in momentum space as x does in ordinary space. Further, Eq. (107) tells us that the operator representation of x in the momentum space is $i\hbar \dfrac{\partial}{\partial p}$.

PROBLEM 2.9

Using the general recipe that the expectation value of an observable characterized by the operator $\mathcal{O}$ is given by

$$\langle \mathcal{O} \rangle = \int \Psi^* \mathcal{O} \Psi \, d\tau \tag{108}$$

prove that

$$\frac{d}{dt} \langle x \rangle = \frac{1}{m} \langle p_x \rangle$$

and

$$\frac{d}{dt} \langle p_x \rangle = -\langle \frac{\partial V}{\partial x} \rangle$$

These equations are referred to as Ehrenfest's theorem.

PROBLEM 2.10

Using Eq. (108) prove that

$$\frac{d}{dt} \langle \mathcal{O} \rangle = i\hbar \int \Psi^* [H, \mathcal{O}] \Psi \, d\tau + \int \Psi^* \frac{\partial \mathcal{O}}{\partial t} \Psi \, d\tau \tag{109}$$

where $[H, \mathcal{O}] = H\mathcal{O} - \mathcal{O}H$ represents the commutator of H and $\mathcal{O}$ and $\partial\mathcal{O}/\partial t$ is due to the explicit time dependence of $\mathcal{O}$. [*Hint*: Differentiate Eq. (108) inside the integral sign and use Eq. (24). You may use the Hermitian nature of H—

See Sec. 8.3 and Solution 8.14 or else substitute for H and integrate by parts as in the solution of Problem 2.9].

PROBLEM 2.11

For the ground state and the first excited state of the harmonic oscillator the wavefunctions are

$$\exp\left[-\frac{m\omega}{2\hbar}x^2\right] \quad \text{and} \quad x\exp\left[-\frac{m\,\omega}{2\hbar}x^2\right]$$

respectively (see Sec. 3.6.3). Show that the values of the uncertainty product $\Delta x\Delta p$ are $\frac{1}{2}\hbar$ and $\frac{3}{2}\hbar$ (see also Sec. 8.9.1).

PROBLEM 2.12

Consider the normalized square wave packet

$$\begin{aligned}\Psi(x) &= \frac{1}{\sqrt{2L}}\exp\left[i\,\frac{p_0x}{\hbar}\right] \qquad && |x| \leqslant L \\ &= 0 && |x| > L\end{aligned} \tag{110}$$

Calculate $a(p)$ and give a physical interpretation of the result.

PROBLEM 2.13

Study the diffraction pattern due to a beam of electrons passing through an infinitely long slit of width $2a$. [*Hint*: You may assume

$$\begin{aligned}\Psi(y, o) &= \frac{1}{\sqrt{2b}} \qquad && \text{for } |y| \leqslant b \\ &= 0 && \text{for } |y| > b\end{aligned} \tag{111}$$

and calculate $a(p_y)$.]

PROBLEM 2.14

Extend the analysis of the previous problem to calculate the diffraction pattern for a double slit.

PROBLEM 2.15

For the momentum space wave function given by

$$\begin{aligned}a(p) &= \frac{1}{(\Delta p)^{1/2}}, \qquad && p_0 - \frac{\Delta p}{2} \leqslant p \leqslant p_0 + \frac{\Delta p}{2} \\ &= 0, && |p - p_0| > \frac{\Delta p}{2}\end{aligned} \tag{112}$$

calculate $\Psi(x)$ and interpret the results physically.

PROBLEM 2.16

(a) For the wave packet given by Eq. (72) show that the wave packet remains undistorted for $t \ll t_0$ where

$$t_0 = \frac{2}{(\Delta k)^2\,\dfrac{d^2\omega}{dk^2}} = \frac{2\hbar}{(\Delta p)^2\,\dfrac{d^2E}{dp^2}} \simeq \frac{2m(\Delta x)^2}{\hbar} \tag{113}$$

where use has to be made of Eq. (66) and the uncertainty relation.

(b) For a particle of mass 10^{-4} gm and localized within $\Delta x \sim 10^{-3}$ cm calculate t_0 and compare its value for an electron localized in a distance of 10^{-8} cm. Interpret the two results physically.

PROBLEM 2.17

Calculate t_0 for the Gaussian wave packet [Eq. (85)] and show that the exact results obtained in Sec. 2.8 are consistent with Eq. (113).

PROBLEM 2.18

Show that for a non-relativistic free particle

$$\Psi(x, t) = \int_{-\infty}^{+\infty} \Psi(x', 0)\, G(x, x', t)\, dx' \tag{114}$$

where

$$G(x, x', t) = \sqrt{\frac{m}{2\pi i \hbar t}} \exp\,[i(x - x')^2 m/2\hbar t] \tag{115}$$

is known as the free particle propagator. What would be $G(x, x', 0)$? Interpret it physically.

PROBLEM 2.19

Consider the three dimensional wave packet describing the motion of a free particle

$$\Psi(x, y, z, 0) = N \exp\left[-\frac{x^2}{2\sigma_1^2} - \frac{y^2}{2\sigma_2^2} - \frac{z^2}{2\sigma_3^2}\right] \exp\left[\frac{i}{\hbar} p_0 x\right] \tag{116}$$

Discuss physically the motion of such a wave packet. Calculate the value of $a(p_x, p_y, p_z)$ and then $\Psi(x, y, z, t)$.

PROBLEM 2.20

Show that the uncertainty product is minimum for a Gaussian wave packet.

PROBLEM 2.21

Consider the three dimensional momentum space wave function

$$a(\mathbf{p}) = N \exp\left[-\frac{|p|}{\Delta p}\right] \tag{117}$$

Calculate $\Psi(\mathbf{r}, 0)$.

SOLUTIONS

SOLUTION 2.1

Assuming a solution of Eq. (13) of the form $\Psi(x, t) = X(x)\, T(t)$ we obtain

$$(2mi\hbar) \frac{1}{T(t)} \frac{dT}{dt} = -\hbar^2 \frac{1}{X(x)} \frac{d^2X}{dx^2} = p^2$$

Thus the variables have indeed separated out and we have set each side equal to a positive constant ($=p^2$); otherwise the wavefunction will tend to an infinite value either for $x \to +\infty$ or $x \to -\infty$. The solutions are $X(x) \sim \exp\left(\frac{i}{\hbar}px\right)$ and $T(t) \sim \exp\left[-\frac{ip^2}{2m\hbar}t\right]$. Since p can take any real value between $-\infty$ and $+\infty$, the general solution of Eq. (13) is given by Eq. (100).

SOLUTION 2.4

Use Eq. (34) to obtain

$$\mathbf{J} = \frac{\hbar k}{m}\frac{1}{r^2}\hat{\mathbf{r}} = \frac{v}{r^2}\hat{\mathbf{r}} \tag{118}$$

which corresponds to a spherical wave whose intensity decreases according to the inverse square law.

SOLUTION 2.5

$$\begin{aligned}\langle p_x\rangle &= -i\hbar\int \Psi^* \frac{\partial\Psi}{\partial x}\,d\tau = -i\hbar\iint dy\,dz\left[\Psi^*\Psi\Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\Psi\frac{\partial\Psi^*}{\partial x}\,dx\right]\\ &= i\hbar\int\Psi\,\frac{\partial\Psi^*}{\partial x}\,d\tau = \langle p_x\rangle^*.\end{aligned} \tag{119}$$

SOLUTION 2.7

$$\Psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty} a(p)\exp\left[\frac{i}{\hbar}px\right]dp \tag{120}$$

Thus

$$\begin{aligned}\langle p\rangle &= -i\hbar\int \Psi^*\,\frac{\partial\Psi}{\partial x}\,dx\\ &= -i\hbar\int_{-\infty}^{+\infty}\Psi^*(x)\left[\frac{1}{(2\pi\hbar)^{1/2}}\int_{-\infty}^{+\infty}\frac{i}{\hbar}p'a(p')\exp\left(\frac{i}{\hbar}p'x\right)dp'\right]dx\\ &= \int_{-\infty}^{+\infty}dp\,a^*(p)\left[\int_{-\infty}^{+\infty}dp'\,p'a(p')\,\delta(p-p')\right]\\ &= \int_{-\infty}^{+\infty}a^*(p)\,p\,a(p)\,dp\end{aligned}$$

where we have used Eq. (3) of Appendix F. Similarly, we can calculate for $\langle p^2\rangle$ and Eq. (105) follows directly from Parseval's theorem (see Appendix D).

SOLUTION 2.8

In Eq. (44) substitute for Ψ and Ψ^* from Eq. (120).

SOLUTION 2.9

Differentiating Eq. (44) we get

$$\frac{d}{dt}\langle x\rangle = \int\left[\Psi^* x\,\frac{\partial\Psi}{\partial t} + \frac{\partial\Psi^*}{\partial t}\,x\Psi\right]d\tau$$
$$= \frac{i\hbar}{2m}\int\left[\Psi^* x\nabla^2\Psi - (\nabla^2\Psi^*)x\Psi\right]d\tau \qquad (121)$$

where use has been made of Eqs. (28) and (29). Now

$$\int(\nabla^2\Psi^*)x\Psi d\tau = \int\nabla\cdot(x\Psi\nabla\Psi^*)d\tau - \int(\nabla\Psi^*)\cdot\nabla(x\Psi)d\tau$$

The first integral on the right can be transformed to a surface integral by use of Gauss theorem and this integral would vanish because a wave packet vanishes at infinity.

Thus

$$\int(\nabla^2\Psi^*)x\,\Psi d\tau = -\int(\nabla\Psi^*)\cdot\nabla(x\Psi)d\tau$$
$$= -\int\nabla\,(\Psi^*\,\nabla x\Psi)d\tau + \int\Psi^*\,\nabla^2(x\Psi)d\tau$$

The first integral on the right again vanishes. Substituting in Eq. (121) we get

$$\frac{d}{dt}\langle x\rangle = \frac{i\hbar}{2m}\int\Psi^*\left[x\nabla^2\Psi - \nabla^2\Big(x\Psi\Big)\right]d\tau$$
$$= \frac{1}{m}\int\Psi^*\left(-i\hbar\,\frac{\partial\Psi}{\partial x}\right)d\tau = \frac{1}{m}\langle p_x\rangle \qquad (122)$$

Using a method similar to that used above we get

$$\frac{d}{dt}\langle p_x\rangle = -i\hbar\int\left[\frac{\partial\Psi^*}{\partial t}\,\frac{\partial\Psi}{\partial x} + \Psi^*\,\frac{\partial}{\partial x}\,\frac{\partial\Psi}{\partial t}\right]d\tau$$
$$= \int\Psi^*\left[V\frac{\partial\Psi}{\partial x} - \frac{\partial}{\partial x}\Big(V\Psi\Big)\right]d\tau = \left\langle -\frac{\partial V}{\partial x}\right\rangle \qquad (123)$$

SOLUTION 2.12

Using Eq. (65) it immediately follows that

$$a(p) = \left(\frac{\hbar}{\pi L}\right)^{\frac{1}{2}}\frac{\sin\left[(p_0-p)L/\hbar\right]}{(p_0-p)} \qquad (124)$$

In Fig. 2.2 we have plotted $|a(p)|^2$ as a function of p. The figure shows that $|a(p)|^2$ is peaked around $p = p_0$ with a width $\hbar\pi/L$. Since $|a(p)|^2\,dp$ represents the probability of finding the momentum between p and $p + dp$, we have $\Delta p \sim \hbar\pi/L$ and since $\Delta x \sim 2L$, we get $\Delta p\,\Delta x \sim \hbar$ consistent with the uncertainty principle.

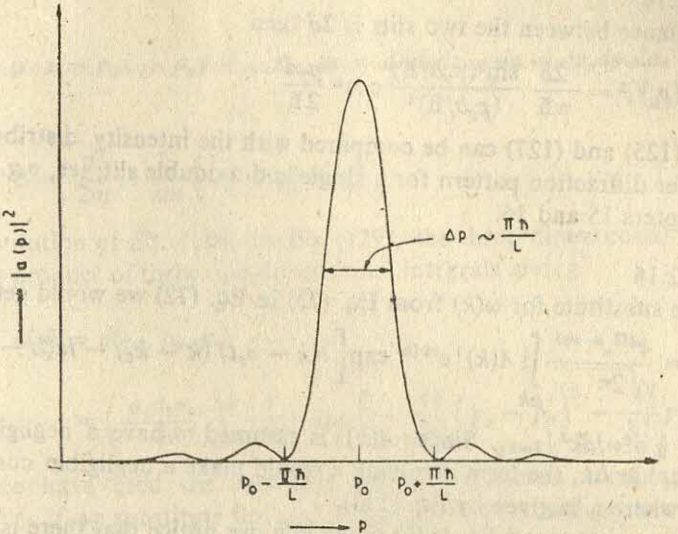

Fig. 2.2 The variation of $|a(p)|^2$ with p for $a(p)$ given by Eq. (123). The function is sharply peaked at $p = p_0$ and has a width $\sim \hbar\pi/L$.

SOLUTION 2.13

Equation (111) corresponds to a wave packet that passes through the slit (Fig. 2.3) at $t = 0$. Now, using Eq. (65) we get

$$|a(p_y)|^2 = \frac{a}{\pi\hbar}\,\frac{\sin^2(p_y b/\hbar)}{(p_y b/\hbar)^2} \tag{125}$$

The above equation represents the intensity distribution on a screen placed normal to the beam beyond the slit; the distance from the centre of the screen being proportional to p_y. Putting $p_y/p \approx \theta$, we get

$$I(\theta) = I_0\,\frac{\sin^2(\theta/\theta_0)}{(\theta/\theta_0)^2} \tag{126}$$

where I_0 is the intensity at $\theta = 0$ and $\theta_0 = \hbar/pb = \lambda/2\pi b$. The above equation represents the single slit diffraction pattern.

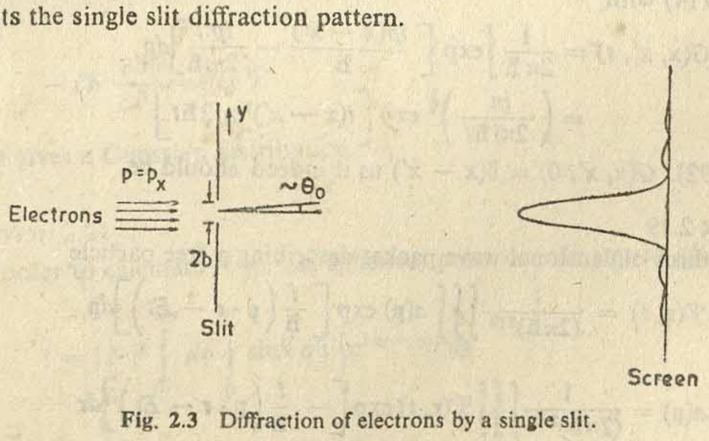

Fig. 2.3 Diffraction of electrons by a single slit.

SOLUTION 2.14

If the distance between the two slits is $2d$ then

$$|a(p_y)|^2 = \frac{2b}{\pi\hbar}\,\frac{\sin^2(p_y b/\hbar)}{(p_y b/\hbar)^2}\cos^2\frac{p_y d}{2\hbar} \tag{127}$$

Equations (125) and (127) can be compared with the intensity distributions in a Fraunhofer diffraction pattern for a single and a double slit; see, e.g., Ghatak (1977) Chapters 15 and 16.

SOLUTION 2.16

(a) If we substitute for $\omega(k)$ from Eq. (73) in Eq. (72) we would get

$$\Psi(x, t) = \frac{e^{i(k_0 x - \omega_0 t)}}{\sqrt{2\pi}}\int_{\Delta k}|A(k)|\,e^{i\varphi(k)}\exp\Big[i(x - v_g t)(k - k_0) - i\alpha(k - k_0)^2 t\Big]dk$$

where $\alpha = \frac{1}{2}\,d^2\omega/dk^2\,|_{k=k_0}$. Since $|A(k)|$ is assumed to have a negligible value for $|k - k_0| \gtrsim \Delta k$, the term involving α would make a negligible contribution for $t \ll t_0$ where t_0 is given by Eq. (113).

In order to understand Eq. (113) physically, we notice that there is a spread $\sim \Delta p$ in the momentum associated with the packet. Thus if we consider two portions of the packet, one corresponding to $p_0 - \Delta p/2 < p < p_0$ and the other corresponding to $p_0 < p < p_0 + \Delta p/2$ then the velocity of the packets will differ by $\Delta p/2m$. Thus there will be distortion in the packet when

$$\frac{t\Delta p}{2m} \approx \Delta x \quad \text{(the initial width of the packet).}$$

The above condition is consistent with Eq. (113).

(b) For $m \approx 10^{-4}$ g, $\Delta x \approx 10^{-3}$ cm, $t_0 \sim 2 \times 10^{17}$ sec $\sim 10^{10}$ years. On the other hand, for an electron with $\Delta x \approx 10^{-8}$ cm, $t_0 \approx 10^{-16}$ sec. Thus for a macroscopic particle the distortion is negligible and hence a classical description is adequate.

SOLUTION 2.18

If we substitute for $a(p)$ from Eq. (65) in Eq. (63) and use Eq. (66) we would get Eq. (114) with

$$G(x, x', t) = \frac{1}{2\pi\hbar}\int\exp\left[\frac{ip(x - x')}{\hbar} - \frac{ip^2 t}{2m\hbar}\right]dp$$
$$= \left(\frac{m}{2\pi i\hbar t}\right)^{\frac{1}{2}}\exp\Big[i(x - x')^2 m/2\hbar t\Big]$$

(see Eq. 92). $G(x, x', 0) = \delta(x - x')$ as it indeed should be.

SOLUTION 2.19

For a three dimensional wave packet describing a free particle

$$\Psi(\mathbf{r}, t) = \frac{1}{(2\pi\hbar)^{3/2}}\iiint a(\mathbf{p})\exp\left[\frac{i}{\hbar}\Big(\mathbf{p}\cdot\mathbf{r} - Et\Big)\right]d\mathbf{p} \tag{128}$$

and

$$a(\mathbf{p}) = \frac{1}{(2\pi\hbar)^{3/2}}\iiint\Psi(\mathbf{r}, t)\exp\left[-\frac{i}{\hbar}\Big(\mathbf{p}\cdot\mathbf{r} - Et\Big)\right]d\mathbf{r} \tag{129}$$

where

$$\mathbf{p}\cdot\mathbf{r} = p_x x + p_y y + p_z z, \quad d\tau = dx\,dy\,dz, \quad d\mathbf{p} = dp_x\,dp_y\,dp_z$$

and

$$E = \frac{p^2}{2m} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

On substitution of Eq. (116) in Eq. (129), the three dimensional integral becomes a product of three one-dimensional integrals giving

$$\begin{aligned} a(\mathbf{p}) &= a(p_x, p_y, p_z) \\ &= \left(\frac{\sigma_1\sigma_2\sigma_3}{\hbar^3}\right)^{\frac{1}{2}} \frac{1}{\pi^{3/4}} \exp\left[-\frac{\sigma_1^2}{2\hbar^2}\left(p_x - p_0\right)^2 - \frac{\sigma_2^2}{\hbar^2}p_y^2 - \frac{\sigma_3^2}{\hbar^2}p_z^2\right] \end{aligned}$$

where we have used the fact that the normalization constant $N = \pi^{-3/4}/(\sigma_1\sigma_2\sigma_3)^{1/2}$. If we substitute for $a(\mathbf{p})$ in Eq. (128) we would get (see Sec. 2.8)

$$\Psi(\mathbf{r}, t)\,|^2 = \frac{1}{\pi^{3/2}[\sigma_1(t)\sigma_2(t)\sigma_3(t)]} \exp\left[-\frac{\left\{x - \frac{p_0}{m}t\right\}^2}{\sigma_1^2(t)}\right] \times$$

$$\exp\left[-\frac{y^2}{\sigma_2^2(t)}\right] \exp\left[-\frac{z^2}{\sigma_3^2(t)}\right]$$

where

$$\sigma_i(t) = \sigma_i\left[1 + \frac{\hbar^2 t^2}{m^2\sigma_i^4}\right]^{\frac{1}{2}}$$

If we assume σ_1 to be very large then there is propagation along the x-axis and spreading along the y and z directions.

Solution 2.20

The uncertainty product is minimum when f is a multiple of g (see Sec. 2.6); thus

$$-i\hbar\,\frac{\partial\Psi}{\partial x} = Cix\,\Psi$$

which gives a Gaussian distribution.

Solution 2.21

In order to calculate N we use spherical polar coordinates to get

$$1 = |N|^2 \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} e^{-2p/\Delta p} p^2\, dp$$

which gives $N = (\Delta p)^{3/2}/\sqrt{\pi}$ Thus

$$\Psi(\mathbf{r}, 0) = \frac{|N|^2}{(2\pi\hbar)^{3/2}} \int_0^{2\pi} d\varphi \int_0^{\infty} p^2 dp \exp\left[-\frac{p}{\Delta p}\right] \int_0^{\pi} \exp\left[-\frac{ipr\cos\theta}{\hbar}\right] \sin\theta \, d\theta$$

where we have assumed p_z to be along $\mathbf{r}$. On carrying out the integration we get

$$\Psi(\mathbf{r}, 0) = \frac{1}{\pi}\left(2r_0\right)^{3/2} \frac{r_0}{(r^2 + r_0^2)^2}$$

where $r_0 = \hbar/\Delta p$.

CHAPTER THREE

Simple Solutions of the Schrödinger Equation I : One Dimensional Considerations

3.1 Stationary States

When the Hamiltonian for a system is independent of time, there is an essential simplification in that the general solution of the Schrödinger equation can be expressed as a function of spatial co-ordinates and a function of time. Thus, assuming the potential energy function to be independent of time, the time dependent Schrödinger equation [see Eq. (22) of Chapter 2]

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\,\Psi(x, t) \tag{1}$$

can be solved by using the method of separation of variables

$$\Psi(x, t) = \psi(x)\, T(t) \tag{2}$$

Substituting in Eq. (1) and dividing by $\Psi(x, t)$, we obtain

$$\frac{i\hbar}{T(t)}\frac{dT}{dt} = \frac{1}{\psi}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi\right] \tag{3}$$

The variables have indeed separated out in the sense that the LHS is a function of time alone while the RHS is a function of space alone; thus each side must be equal to a constant, say E. We have therefore

$$\frac{i\hbar}{T}\frac{dT}{dt} = \frac{1}{\psi}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi\right] = E \tag{4}$$

or

$$T(t) = e^{-iEt/\hbar} \tag{5}$$

and

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \tag{6}$$

so that the solution can be written as

$$\Psi(x, t) = \psi(x)\, e^{-iEt/\hbar} \tag{7}$$

The probability density is given by

$$\rho = |\,\Psi(x, t)\,|^2 = |\,\psi(x)\,|^2 \tag{8}$$

Now, Eq. (6) can be written as

$$H\psi(x) = E\psi(x) \tag{9}$$

where

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) = \frac{p^2}{2m} + V(x) \tag{10}$$

represents the Hamiltonian operator and E is a *number*. Equation (9) is an eigenvalue equation and E is the energy eigenvalue. In general, the eigenvalues can have a discrete set along with a continuous range of eigenvalues and the general solution of Eq. (1) is of the form

$$\Psi(x, t) = \sum_n a_n \psi_n(x)\, e^{-iE_n t/\hbar} \tag{11}$$

where $\psi_n(x)$ are the eigenfunctions of H and E_n are the corresponding energy eigenvalues; a_n are constants which can be determined from the form of $\Psi(x, 0)$. In Eq. (11), Σ denotes a summation over the discrete states and integration over the continuum states.

Now, a state with well defined energy has a wavefunction of the form given by Eq. (7) and for such a state the probability density [see Eq. (8)] is independent of time [this follows from the fact that E is always real, see Eq. (18)]. Such states are therefore known as *stationary states*. The time independent part of the wavefunction $\psi(x)$, for a stationary state, satisfies Eq. (6) which may be rewritten in the form

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left[E - V(x)\right]\psi(x) = 0 \tag{12}$$

which is known as the one-dimensional time independent Schrödinger equation.

In Sec. 3.2 we will discuss two theorems regarding the boundary and continuity conditions of the wavefunction. In Secs. 3.3 and 3.4 we will discuss the degeneracy of a state and the orthogonality of the eigenfunctions and in Sec. 3.5 we will discuss the parity of the eigenfunctions. In Sec. 3.6 we will give the solution of the Schrödinger equation for four problems of practical interest.

3.2 Boundary and Continuity Conditions

Since the wavefunction ψ is to be interpreted as the probability amplitude, ψ should be single valued and $|\psi(x)|^2\, dx$ has to be finite for finite values of dx. Therefore

$$\underset{dx \to 0}{\text{Lt}}\ |\psi|^2\, dx = 0 \tag{13}$$

In practice, this condition is satisfied by demanding that ψ be finite everywhere; but this is not a necessary requirement in some cases. We shall discuss this in more detail in Sec. 5.3. For the problems we discuss now, we need only assume that ψ is finite everywhere. Further, we have the following two theorems.

Theorem 1

The derivative of the wavefunction $d\psi/dx$ is always continuous as long as the potential energy $V(x)$ is finite, whether or not it is continuous*.

---

*It may be mentioned that in many texts the continuity of ψ and $d\psi/dx$ are taken to be axioms. This is not correct because it follows from the fact that $\psi(x)$ satisfies a second order differential equation [Eq. (12)] Indeed, when $V(x)$ becomes infinite, $d\psi/dx$ is *not* continuous see Sec. 3.6.1).

Proof

We integrate the Schrödinger equation [Eq. (12)] from $x - \varepsilon$ to $x + \varepsilon$ to obtain

$$\int_{x-\varepsilon}^{x+\varepsilon} \frac{d^2\psi}{dx^2}\, dx = -\frac{2m}{\hbar^2} \int_{x-\varepsilon}^{x+\varepsilon} [E - V(x)]\, \psi(x)dx$$

or

$$\psi'(x+\varepsilon) - \psi'(x-\varepsilon) = -\frac{2m}{\hbar^2} \int_{x-\varepsilon}^{x+\varepsilon} [E - V(x)]\, \psi(x)dx$$

Since $V(x)$ is assumed to be finite (it could, however, be discontinuous), the RHS tends to zero as $\varepsilon \to 0$. Thus ψ' is continuous at any value of x. It is obvious that ψ has to be necessarily continuous everywhere.

Theorem 2

If the potential energy function $V(x)$ is infinite anywhere; the proper boundary condition is obtained by assuming $V(x)$ to be finite at that point and carrying out a limiting process making $V(x)$ tend to infinity. Such a limiting process makes the wavefunction vanish at a point where $V(x) = \infty$ (see Problem 3.2).

3.3 Degeneracy

If there are more than one linearly independent wavefunctions belonging to the same energy level E, the energy level is said to be degenerate. If there are g linearly independent wavefunctions ($\psi_1, \psi_2 \ldots \psi_g$) belonging to the same energy state then the energy level is said to be g-fold degenerate. It can be easily shown that any linear combination of the degenerate wavefunctions

$$\psi = c_1\psi_1 + c_2\psi_2 + \ldots + c_g\psi_g$$

is also an eigenfunction belonging to the same energy eigenvalue. We will prove this for $g = 2$, the generalization is straightforward. Since ψ_1 and ψ_2 are eigenfunctions belonging to same eigenvalue E_1, we have [see Eq. (6)]

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} + V(x)\psi_1 = E_1\psi_1$$

and

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V(x)\,\psi_2 = E_1\psi_2$$

If we multiply the first equation by c_1 and the second equation by c_2 and add, we would get

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}(c_1\psi_2 + c_2\psi_2) + V(x)(c_1\psi_1 + c_2\psi_2) = E_1(c_1\psi_1 + c_2\psi_2)$$

which shows that the linear combination $c_1\psi_1 + c_2\psi_2$ is also an eigenfunction belonging to the *same* eigenvalue E_1.

3.4. Orthogonality of Eigenfunctions

We shall first prove that all energy eigenvalues E_n are real and that if $E_n \neq E_k$, the corresponding eigenfunctions are necessarily orthogonal. We write the one dimensional Schrödinger equation for the two states corresponding to the eigenvalues E_n and E_k

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} + V(x)\,\psi_n = E_n\psi_n \tag{14}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_k}{dx^2} + V(x)\,\psi_k = E_k\psi_k \tag{15}$$

If we multiply Eq. (14) by ψ_k^* and multiply the complex conjugate of Eq. (15) by ψ_n and subtract, we would get

$$-\frac{\hbar^2}{2m}\left[\psi_k^*\frac{d^2\psi_n}{dx^2} - \psi_n\frac{d^2\psi_k^*}{dx^2}\right] = (E_n - E_k^*)\,\psi_k^*\psi_n$$

or

$$-\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\frac{d}{dx}\left[\psi_k^*\frac{d\psi_n}{dx} - \psi_n\frac{d\psi_k^*}{dx}\right]dx = (E_n - E_k^*)\int_{-\infty}^{\infty}\psi_k^*\,\psi_n\,dx \tag{16}$$

The left hand side is simply

$$-\frac{\hbar^2}{2m}\left[\psi_k^*\frac{d\psi_n}{dx} - \psi_n\frac{d\psi_k^*}{dx}\right]\Bigg|_{-\infty}^{+\infty}$$

which would vanish if the wavefunctions are assumed to vanish at infinity. Thus we get

$$(E_n - E_k^*)\int_{-\infty}^{+\infty}\psi_k^*\,\psi_n\,dx = 0 \tag{17}$$

If $k = n$, then since $\int_{-\infty}^{\infty}|\psi_n|^2\,dx$ is necessarily positive*, we must have

$$E_n = E_n^* \tag{18}$$

proving that all eigenvalues are real. Further, for $E_n \neq E_k$

$$\int_{-\infty}^{\infty}\psi_k^*\,\psi_n\,dx = 0 \tag{19}$$

which represents the orthogonality condition.

---

*Except in the trivial case when the wavefunction vanishes everywhere.

If $E_k = E_n$, i.e., if there are two (or more) wavefunctions belonging to the same eigenvalue then the corresponding wavefunctions are not necessarily orthogonal. Since any linear combination of degenerate state wavefunctions are also possible eigenfunctions (see Sec: 3.3) one can always construct suitable linear combinations which are mutually orthogonal (see Problem 3.3).

Since the Schrödinger equation is a linear equation, if ψ is a solution, $c\,\psi$ is also a solution where c is an arbitrary complex number. One can always choose the constant such that

$$\int_{-\infty}^{\infty} |\psi_n|^2 \, dx = 1 \tag{20}$$

which is the normalization condition. Equations (19) and (20) can be combined to write it in the form

$$\int_{-\infty}^{\infty} \psi_k^* \psi_n \, dx = \delta_{kn} \tag{21}$$

where δ_{kn} is the Kronecker delta function defined through the equation

$$\begin{aligned} \delta_{kn} &= 0 \qquad k \neq n \\ &= 1 \qquad k = n \end{aligned} \tag{22}$$

Equation (21) is known as the orthonormality condition.

3.5 Parity

In this section we will show that if

$$V(x) = V(-x) \tag{23}$$

i.e., if the potential energy function is symmetric about $x = 0$ then the eigenfunctions of the Schrödinger equation are either symmetric functions of x $[\psi(x) = \psi(-x)]$ or antisymmetric functions* of x $[\psi(x) = -\psi(-x)]$. In order to prove this we first write the Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x) = E\,\psi(x) \tag{24}$$

Making the transformation $x \rightarrow -x$ we get

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\,\psi(-x) + V(x)\,\psi(-x) = E\,\psi(-x) \tag{25}$$

where we have used the fact that $V(-x) = V(x)$. Comparing Eqs. (24) and (25) we see that $\psi(x)$ and $\psi(-x)$ are eigenfunctions belonging to the same energy E.

---

*This theorem is strictly true for non degenerate states only. For degenerate states the wavefunctions need not be symmetric or antisymmetric functions of x. However, even for degenerate states one can always construct appropriate linear combinations which are either symmetric or antisymmetric functions of x.

Thus, if the state is non-degenerate then $\psi(-x)$ must be a multiple of $\psi(x)$

$$\psi(-x) = \lambda\, \psi(x)$$

Clearly

$$\psi(x) = \lambda\, \psi(-x) = \lambda^2 \psi(x)$$

so that $\lambda^2 = 1$ or $\lambda = \pm 1$. Hence

$$\psi(-x) = \pm \psi(x) \tag{26}$$

proving the theorem. The eigenfunctions which belong to the class $\lambda = +1$ are said to have even *parity* and those with $\lambda = -1$ to have odd parity.

For a degenerate state $\psi(-x)$ need not be a multiple of $\psi(x)$. Indeed if $\psi(-x)$ is not a multiple of $\psi(x)$ then from Eqs. (24) and (25) it immediately follows that $\psi(-x)$ must be another independent solution corresponding to the same energy level. Further, any linear combination of $\psi(x)$ and $\psi(-x)$ could also be a possible eigenfunction (see Sec. 3.3) and we can always choose linear combinations

$$[\psi(x) + \psi(-x)] \quad \text{and} \quad [\psi(x) - \psi(-x)]$$

which are symmetric and antisymmetric functions of x respectively. Thus even for degenerate states one can always choose appropriate linear combinations which have definite *parity*, i.e., they are either symmetric or antisymmetric functions of x.

3.6 Some Exact Solutions of the One Dimensional Schrödinger Equation

In this section we will consider four potential energy distributions for which exact solutions of the Schrödinger equation will be obtained. These results have applications in many areas, e.g., in theory of metals, quantum theory of radiation, etc.

In Sec. 3.6.1 we will consider a particle inside an infinitely deep potential well which will be followed by considering the effects of the potential well of finite depth. In Sec. 3.6.3 we will consider the linear harmonic oscillator problem and in Sec. 3.6.4 we will consider the double well problem.

3.6.1 Particle in a One-Dimensional Infinitely Deep Potential Well

We will determine the energy levels and the corresponding eigenfunctions of a particle of mass μ in a one-dimensional infinitely deep potential well characterised by the potential energy variation of the form

$$\begin{aligned} V(x) &= 0 \quad \text{for} \quad 0 < x < a \\ &= \infty \quad \text{for} \quad x < 0 \text{ and for } \quad x > a \end{aligned} \tag{27}$$

(The corresponding three dimensional problem is discussed in Problem 5.2). For $0 < x < a$, the one-dimensional Schrödinger equation becomes

$$\frac{d^2\psi}{dx^2} + k^2\psi(x) = 0 \tag{28}$$

where

$$k^2 = \frac{2\mu E}{\hbar^2} \tag{29}$$

The general solution of this equation is

$$\psi = A \sin kx + B \cos kx$$

Since the boundary condition at a surface at which there is an infinite potential step is that ψ is zero (see Sec. 3.2, Theorem 2), we must have

$$\psi(x = 0) = \psi(x = a) = 0 \tag{30}$$

The above condition also follows from the fact that since the particle is inside an infinitely deep potential well, it is always confined in the region $0 < x < a$ and therefore ψ must vanish for $x < 0$ and $x > L$; and for ψ to be continuous, Eq. (30) must be satisfied. Using the boundary condition given by Eq. (30), we get

$$\psi(x = 0) = B = 0$$

and

$$\psi(x = a) = A \sin ka = 0$$

Thus, either

$$A = 0$$

or

$$ka = n\pi, \quad n = 1, 2, \ldots \tag{31}$$

The condition $A = 0$ leads to the trivial solution of ψ vanishing everywhere, the same is the case for $n = 0$. Thus the allowed energy levels are given by

$$E_n = \frac{\pi^2 n^2 \hbar^2}{2\mu a^2}, \quad n = 1, 2, 3, \ldots \tag{32}$$

The corresponding eigenfunctions are

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) \quad (0 < x < a) \tag{33}$$

where the factor $\sqrt{2/a}$ is such that the wavefunctions form an orthonormal set [cf. Eq. (21)]

$$\int_0^a \psi_m^*(x)\, \psi_n(x)\, dx = \delta_{mn} \tag{34}$$

It may be noted that whereas $\psi_n(x)$ is continuous everywhere, $d\psi_n(x)/dx$ is discontinuous at $x = 0$ and at $x = a$. This is because of $V(x)$ becoming infinite at $x = 0$ and at $x = a$ (see Sec. 3.2). Figure 3 1 gives a plot of the first three eigenfunctions and one can see that the eigenfunctions are either symmetric or antisymmetric about the line $x = a/2$; this follows from the fact that $V(x)$ is symmetric about $x = a/2$ (see Sec. 3.5).

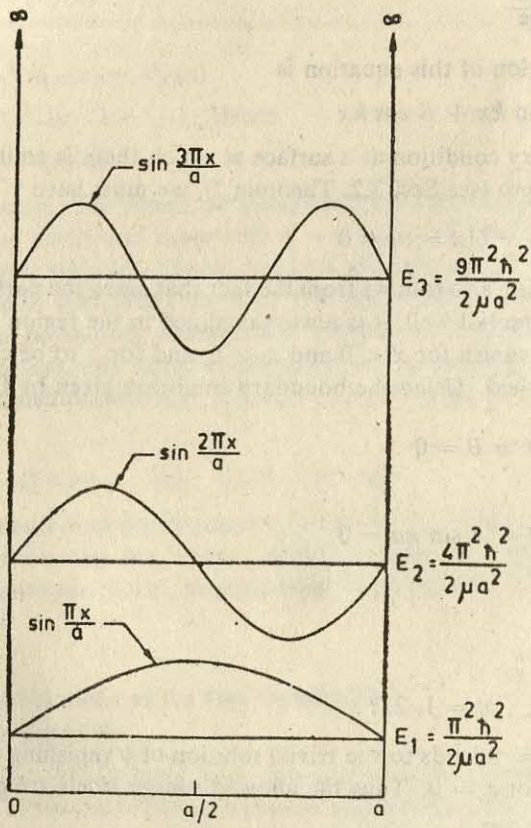
∞
∞
sin $\frac{3\pi x}{a}$
$E_3 = \frac{9\pi^2\hbar^2}{2\mu a^2}$
sin $\frac{2\pi x}{a}$
$E_2 = \frac{4\pi^2\hbar^2}{2\mu a^2}$
sin $\frac{\pi x}{a}$
$E_1 = \frac{\pi^2\hbar^2}{2\mu a^2}$
0
a/2
a

Fig. 3.1 The energy eigenvalues and eigenfunctions for a particle in an infinitely deep potential well. Notice that the eigenfunctions are either symmetric or antisymmetric about $x = a/2$.

It can easily be seen that E cannot be negative because then the boundary conditions at $x = 0$ *and* at $x = a$ cannot be simultaneously satisfied (see Problem 3.1).

Finally, the eigenfunctions given by Eq. (33) form a complete set, i.e., an arbitrary (well behaved) function which satisfies the same boundary conditions (viz., vanishing at $x = 0$ and at $x = a$) can be expanded in terms of the eigenfunctions of H

$$\phi(x) = \sum C_n\psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1,2,\ldots} c_n \sin\left(\frac{n\pi}{a}x\right) \tag{35}$$

where $\phi(x)$ is an arbitrary well behaved function (with $\phi(0) = \phi(a) = 0$) and c_n are constants which can be determined by multiplying both sides of the above equation by $\psi_m^*(x)$ and integrating from 0 to a to obtain

$$\int_0^a \psi_m^*(x)\,\phi(x)\,dx = \sum_n c_n \int_0^a \psi_m^*\,\psi_n(x)\,dx = \sum_n c_n\,\delta_{mn} = c_m \tag{36}$$

where we have used the orthonormality condition [Eq. (34)]. Equation (35) may be compared with the Fourier series (see Appendix D).

3.6.2 PARTICLE IN A ONE-DIMENSIONAL POTENTIAL WELL OF FINITE DEPTH

We next consider the square well potential (Fig. 3.2)

$$\begin{aligned} V(x) &= 0 \qquad \text{for} \quad -\frac{a}{2} < x < \frac{a}{2} \\ &= V_0 \qquad \text{for} \quad |x| > a/2 \end{aligned} \tag{37}$$

We first look for solutions corresponding to $E < V_0$. The Schrödinger equation can then be written in the form

$$\begin{aligned} \frac{d^2\psi}{dx^2} + k^2\psi(x) &= 0 \qquad \text{for} \quad |x| < \frac{a}{2} \\ \frac{d^2\psi}{dx^2} - \kappa^2\psi(x) &= 0 \qquad \text{for} \quad |x| > \frac{a}{2} \end{aligned} \tag{38}$$

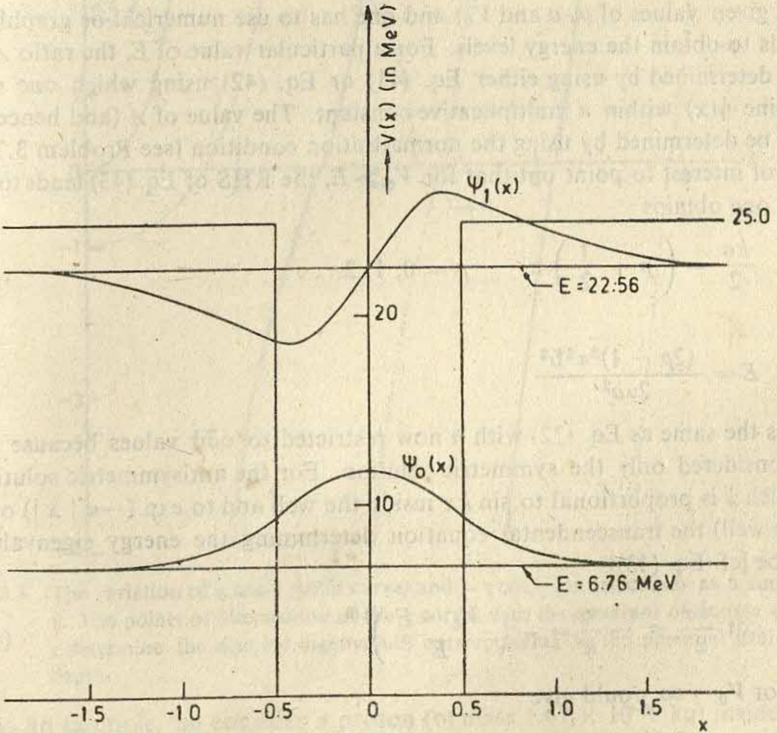

Fig. 3.2 A potential well of finite depth. The eigenvalues and eigenfunctions correspond to $\alpha = 2.0$.

where

$$k^2 \equiv \frac{2\mu E}{\hbar^2} \quad \text{and} \quad \kappa^2 \equiv \frac{2\mu}{\hbar^2}(V_0 - E) \tag{39}$$

Since $V(-x) = V(x)$, the solutions are either symmetric or antisymmetric in x. Corresponding to the symmetric solution we may write

$$\begin{aligned} \psi(x) &= A \cos kx & |x| < a/2 \\ &= B \exp[-\kappa |x|] & |x| > a/2 \end{aligned} \tag{40}$$

where in the region $|x| > a/2$, we have rejected the solution $\exp[\kappa |x|]$ because then $\psi(x)$ will go to infinity as $|x| \to \infty$. Continuity of ψ and $d\psi/dx$ (see Sec. 3.2) at $x = a/2$ leads to

$$A \cos ka/2 = B \exp[-\kappa(a/2)] \tag{41}$$

and

$$-Ak \sin ka/2 = -B\kappa \exp[-\kappa(a/2)] \tag{42}$$

For non-trivial solutions one gets

$$\tan \frac{ka}{2} = \frac{\kappa}{k} = \left[\frac{V_0 - E}{E}\right]^{1/2} \tag{43}$$

The roots of the transcendental equation (43) determine the discrete values of E (for given values of μ, a and V_0) and one has to use numerical or graphical methods to obtain the energy levels. For a particular value of E, the ratio A/B can be determined by using either Eq. (41) or Eq. (42) using which one can determine $\psi(x)$ within a multiplicative constant. The value of A (and hence of B) can be determined by using the normalisation condition (see Problem 3.7).

It is of interest to point out that for $V_0 \gg E$, the RHS of Eq. (43) tends to ∞ so that one obtains

$$\frac{ka}{2} = \left(p + \frac{1}{2}\right)\pi, \qquad p = 0, 1, 2 \ldots$$

or

$$E = \frac{(2p+1)^2 \pi^2 \hbar^2}{2\mu a^2}$$

which is the same as Eq. (32) with n now restricted to odd values because we have considered only the symmetric solution. For the antisymmetric solution (for which ψ is proportional to $\sin kx$ inside the well and to $\exp(-\kappa |x|)$ outside the well) the transcendental equation determining the energy eigenvalues would be [cf. Eq. (43)]

$$\cot \frac{ka}{2} = -\frac{\kappa}{k} = -\left(\frac{V_0 - E}{E}\right)^{1/2} \tag{44}$$

which for $V_0 \to \infty$ would give

$$E = \frac{(2p)^2 \pi^2 \hbar^2}{2\mu a^2}; \qquad p = 1, 2, 3 \ldots$$

Equations (43) and (44) can be put in the more convenient form

$$\eta \tan \eta = (\alpha^2 - \eta^2)^{1/2} \qquad \text{(symmetric case)} \qquad (45)$$

$$-\eta \cot \eta = (\alpha^2 - \eta^2)^{1/2} \qquad \text{(antisymmetric case)} \qquad (46)$$

where $\eta = ka/2 = (2\mu\, Ea^2/4\hbar^2)^{1/2}$ and $\alpha = (2\mu\, V_0 a^2/4\hbar^2)^{1/2}$. For a given value of α, the RHS is a portion of a circle and therefore the roots can easily be determined using numerical methods. In Fig 3.3 we have plotted the functions $\eta \tan \eta$ (solid curve) and $-\eta \cot \eta$ (dotted curve) as a function of η. Their points of intersection with the portion of the circle determines the eigenvalues. It is easy to see that for $0 < \alpha < \pi$ there will be one symmetric state, for $\pi \leqslant \alpha < 2\pi$ there will be two and for $2\pi \leqslant \alpha < 3\pi$ there will be three symmetric states and so on. Similarly for $0 < \alpha < \pi/2$ there will be no antisymmetric state, for $\pi/2 \leqslant \alpha < 3\pi/2$, there will be one antisymmetric state, etc.

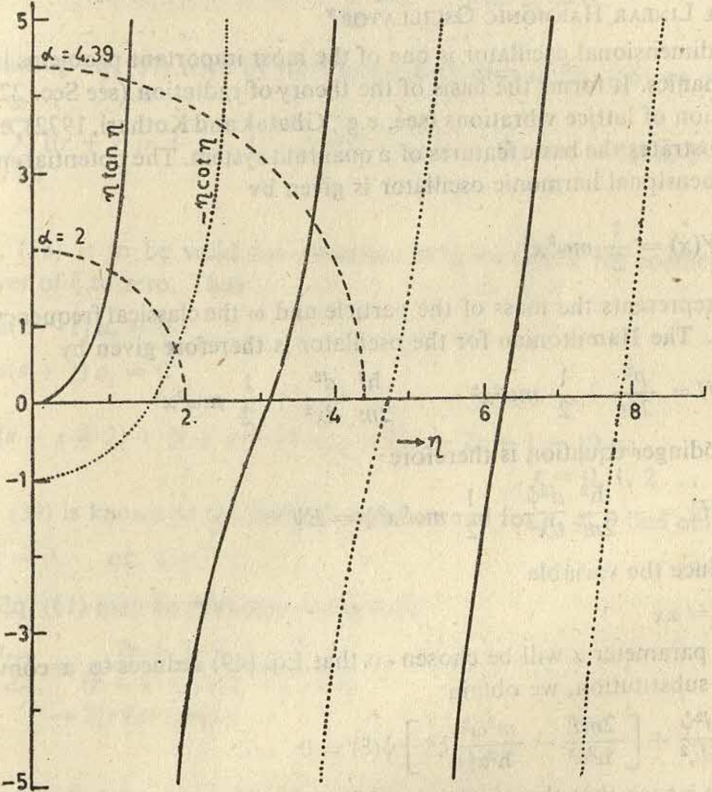

Fig 3.3. The variation of $\eta \tan \eta$ (solid curve) and $-\eta \cot \eta$ (dotted curve) as a function of η. The points of intersection of these curves with the quadrant of a circle of radius α determine the discrete eigenvalues corresponding to the potential well of finite depth.

As an example, we consider a proton (of mass 1.67×10^{-27} kg) inside a one-dimensional well with $V_0 \simeq 25$ MeV $\simeq 4 \times 10^{-12}$J and $a \simeq 3.65 \times 10^{-13}$ cm. Thus

$$\alpha = \left(\frac{2\mu V_0 a^2}{4\hbar^2} \right)^{1/2} \simeq 2.0$$

Since $\alpha < \pi$, there will be one symmetric state and one antisymmetric state; the corresponding energy eigenvalues are 6.76 MeV and 22.56 MeV (see Fig. 3.2).

Till now we have assumed $E < V_0$; had we considered values of $E > V_0$, we would have found that all values of E (greater than V_0) could be possible, i.e., the energy eigenvalues would be continuously distributed in the domain $V_0 < E < \infty$. However, the wavefunction would not have vanished at large distances from the origin—see Chapter 4. Such solutions are of great importance in connection with the scattering of a particle by a force field (see Chapter 19), where the energy is specified in advance and the behaviour of wavefunction at great distances is found in terms of energy.

3.6.3 THE LINEAR HARMONIC OSCILLATOR*

The one-dimensional oscillator is one of the most important problems in quantum mechanics. It forms the basis of the theory of radiation (see Sec. 22.3), the quantization of lattice vibrations (see, e.g., Ghatak and Kothari, 1972), etc., and it also illustrates the basic features of a quantum system. The potential energy of a one-dimensional harmonic oscillator is given by

$$V(x) = \frac{1}{2} m\omega^2 x^2 \tag{47}$$

where m represents the mass of the particle and ω the classical frequency of the oscillator. The Hamiltonian for the oscillator is therefore given by

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 \tag{48}$$

The Schrödinger equation is therefore

$$H\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi = E\psi \tag{49}$$

We introduce the variable

$$\xi = \alpha x \tag{50}$$

where the parameter α will be chosen so that Eq. (49) reduces to a convenient form. On substitution, we obtain

$$\frac{d^2\psi}{d\xi^2} + \left[\frac{2mE}{\hbar^2\alpha^2} - \frac{m^2\omega^2}{\hbar^2\alpha^4} \xi^2 \right] \psi(\xi) = 0 \tag{51}$$

We choose α such that the coefficient of ξ^2 is unity; i.e.,

$$\alpha = \left(\frac{m\omega}{\hbar} \right)^{1/2} \tag{52}$$

Thus the Schrödinger equation becomes

$$\frac{d^2\psi}{d\xi^2} + (\mathcal{E} - \xi^2)\, \psi(\xi) = 0 \tag{53}$$

---

*The harmonic oscillator problem is also discussed in Chapter 8 using the bra and ket notation.

where

$$\mathcal{E} = \frac{2mE}{\hbar^2\alpha^2} = \frac{2E}{\hbar\omega} \tag{54}$$

In order to obtain an exact solution of Eq. (53), we introduce the function $u(\xi)$ defined through the relation*

$$\psi(\xi) = \exp\left(-\frac{\xi^2}{2}\right)u(\xi) \tag{55}$$

Substituting Eq. (55) in Eq. (53), we obtain

$$\frac{d^2u}{d\xi^2} - 2\xi\frac{du}{d\xi} + (\mathcal{E} - 1)\,u(\xi) = 0 \tag{56}$$

We seek a solution of this equation in the form of a power series

$$u = \xi^s(a_0 + a_1\xi + \ldots) = \sum_r a_r\xi^{r+s} \quad \text{with } a_0 \neq 0 \tag{57}$$

Differentiating Eq. (57) term by term and substituting in Eq. (56) we obtain

$$\sum_{r=0}^{\infty} [(r+s)(r+s-1)\,a_r\,\xi^{r+s-2} - \{2(r+s) - (\mathcal{E}-1)\}\,a_r\,\xi^{r+s}] = 0 \tag{58}$$

Since Eq. (58) is to be valid for all values of ξ, we equate the coefficients of each power of ξ to zero. Thus

$$s(s-1)\,a_0 = 0 \tag{59}$$

$$s(s+1)\,a_1 = 0 \tag{60}$$

and

$$(r+s+2) + (r+s+1)\,a_{r+2} = (2r + 2s + 1 - \mathcal{E})\,a_r; \quad r = 0, 1, 2\ldots \tag{61}$$

Equation (59) is known as the indicial equation and for $a_0 \neq 0$ one obtains

$$s = 0 \quad \text{or} \quad s = 1 \tag{62}$$

Further, Eq. (61) may be rewritten in the form

$$\frac{a_{r+2}}{a_r} = \frac{2r + 2s + 1 - \mathcal{E}}{(r+s+2)(r+s+1)} \tag{63}$$

$$\rightarrow 2/r \text{ for large } r$$

---

*If we look at the behaviour of Eq. (53) in the region $\xi^2 \gg \mathcal{E}$ we see that

$$\psi \sim \xi^n \exp(\pm\xi^2/2)$$

indeed satisfies Eq. (53) because

$$\frac{d^2\psi}{d\xi^2} = \left(1 \pm \frac{2n+1}{\xi^2} + \frac{n(n-1)}{\xi^4}\right)\xi^{n+2}\,e^{\pm\xi^2/2} \rightarrow \xi^{n+2}\,e^{\pm\xi^2/2} = \xi^2\psi \text{ (for large } \xi).$$

This suggests that it might be possible to find an exact solution of Eq. (53) of the form given by Eq. (55). We reject the solution with positive exponent because then the solution would diverge as $\xi \rightarrow \pm\infty$.

Now

$$e^{\xi^2} = 1 + \xi^2 + \frac{\xi^4}{2!} + \ldots \tag{64}$$

$$= \sum_{r=0,\,2,\,4\,\ldots} b_r \xi^r,\; b_r = 1\Big/\left(\frac{r}{2}\right)! \;(r \text{ even})$$

Hence

$$\frac{b_{r+2}}{b_r} = \frac{1\Big/\left(\frac{r+2}{2}!\right)}{1\Big/\frac{r}{2}!} = \frac{1}{\frac{r}{2}+1} \rightarrow \frac{2}{r} \quad \text{for large } r$$

Thus, the ratio a_{r+2}/a_r is the same as that of the coefficients of ξ^{r+2} and ξ^r in the expansion of e^{ξ^2}. This means that if the series given by Eq. (57) is allowed to run to an unlimited number of terms, the wavefunction [see Eq. (55)] will behave as $\exp(\xi^2/2)$ for large* ξ and therefore would diverge** for $\xi \rightarrow \pm\infty$. This behaviour can be averted if beyond a certain coefficient a_r, the series is terminated; we can do this by setting

$$a_1 = 0 \qquad (\text{and therefore } a_3 = a_5 = \ldots = 0)$$

and

$$2r + 2s + 1 - \mathcal{E} = 0 \tag{65}$$

We see from Eq. (61) that all coefficients a_{r+2}, a_{r+4}, etc., will then vanish. Since $s = 0$ or 1, we have

$$\mathcal{E} = 2n + 1; \qquad n = 0, 1, 2 \ldots \tag{66}$$

or

$$E = (n + \tfrac{1}{2})\,\hbar\omega \tag{67}$$

Thus the energy eigenvalues are $\frac{1}{2}\hbar\omega$, $\frac{3}{2}\hbar\omega$, $\frac{5}{2}\hbar\omega$, ... ; one again obtains quantized energy levels. The finite value of the ground state energy level $\frac{1}{2}\hbar\omega$, which is called the *zero point energy*, is characteristic of quantum mechanics and is related to the uncertainty principle [see Sec. 1.7].

In order to determine the corresponding eigenfunctions we rewrite $u(\xi)$ [see Eq. (57)] in the form

$$u(\xi) = \xi^s\,[\{a_0 + a_2\xi^2 + a_4\xi^4 + \ldots\} + \{a_1\xi + a_3\xi^3 + \ldots\}] \tag{68}$$

For a particular value of $\mathcal{E}$, only one of the series can be terminated and since $a_0 \neq 0$, we must choose $a_1 = 0$. Thus the value of r given by Eq. (65) must necessarily be even. As an example, we consider the case $n = 2$ for which $\mathcal{E} = 2n + 1 = 5$, thus from Eq. (65)

$$2r + 2s = 4$$

---

*This follows from the fact that only for large values of ξ will the large r terms dominate in the expansion and only then the infinite series will behave as $\exp(\xi^2)$.

**It may be noted that both the infinite series [Eqs. (57) and (64)] are convergent for *all* values of ξ. They only tend to ∞ as $\xi \rightarrow \pm\infty$.

Consequently, we must choose $s = 0$, and the series will terminate at $r = 2$. Further

$$\frac{a_2}{a_0} = \frac{1-5}{2 \times 1} = -2; \quad a_4 = a_6 = \ldots = 0$$

giving

$$u(\xi) = a_0\,[1 - 2\xi^2] \tag{69}$$

Similarly one can determine the other solutions. For $n = 0, 2, 4, \ldots$ we must assume $s = 0$ and for $n = 1, 3, 5, \ldots$ we must assume $s = 1$; the resulting polynomial will be of nth degree. Alternatively, one can argue that for $\mathcal{E}$ given by Eq. (66), Eq. (56) becomes

$$\frac{d^2u}{d\xi^2} - 2\xi\,\frac{du}{d\xi} + 2n\,u(\xi) = 0 \tag{70}$$

and, for each integral value of n, this equation has a solution $H_n(\xi)$, a *polynomial** of nth degree called the Hermite polynomial (see Appendix G). Further, it can be shown that

$$H_n(\xi) = (-1)^n \exp\,(\xi^2)\,\frac{d^n}{d\xi^n} \exp\,(-\xi^2) \tag{71}$$

The normalized harmonic oscillator wavefunctions are

$$\psi_n(x) = N_n \exp\,(-\tfrac{1}{2}\,\xi^2)\,H_n(\xi) = N_n \exp\,(-\tfrac{1}{2}\,\alpha^2x^2)\,H_n(\alpha x) \tag{72}$$

$$N_n = \left[\frac{\alpha}{\sqrt{\pi}\,2^n n!}\right]^{\frac{1}{2}}; \quad \xi = \alpha x = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} x \tag{73}$$

satisfying the normalization condition given by Eq. (21). The first four Hermite polynomials are

$$H_0 = 1; \quad H_1(\xi) = 2\xi; \quad H_2(\xi) = 4\xi^2 - 2; \quad H_3(\xi) = 8\xi^3 - 12\xi \tag{74}$$

In Fig. 3.4 we have plotted $\psi_0(\xi)$, $\psi_1(\xi)$, $\psi_2(\xi)$ as a function of ξ ($= \alpha x$). Notice that ψ_0 and ψ_2 are symmetric in ξ and ψ_1 and ψ_3 are antisymmetric in ξ. Further since $|\psi(x)|^2\,dx$ ($= 1/\alpha\,|\psi(\xi)|^2\,d\xi$) represents the probability of finding the particle between x and $x + dx$ (or between ξ and $\xi + d\xi$), we have plotted in Figs. 3.5 and 3.6 the probability distribution function

$$P(\xi) = \frac{1}{\alpha}\,|\psi(\xi)|^2 \tag{75}$$

as a function of ξ for $n = 0$ and $n = 10$. The dashed curves represent the corresponding classical distribution (see Problem 3.9) which goes to infinity at the end points where the particle has zero velocity. The area under both the curves is unity. The following two points may be noted: (i) according to quantum mechanics, there is a finite probability of finding the particle outside the classically confined region and (ii) for large values of n (if we average over the rapid

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*The other solution would be an infinite series which would behave as $\exp\,(\xi^2)$ for large ξ. For n not equal to an integer both solutions will behave as $\exp\,(\xi^2)$ for $\xi \to \pm\infty$.

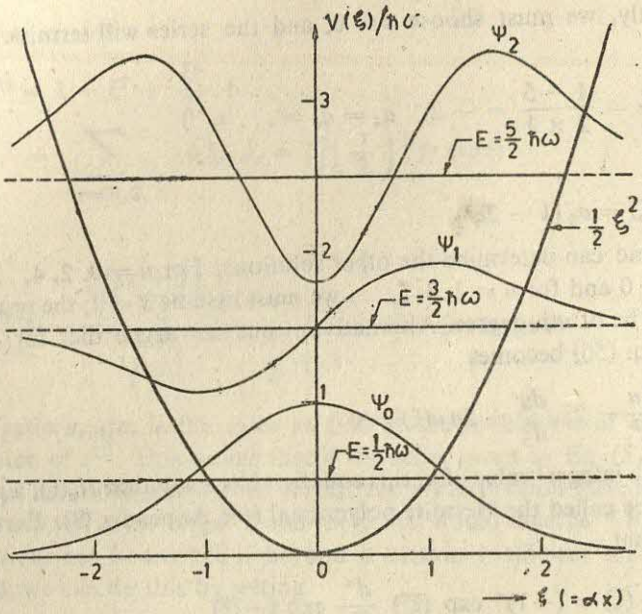

Fig. 3.4 The oscillator potential and the first three eigenfunctions.

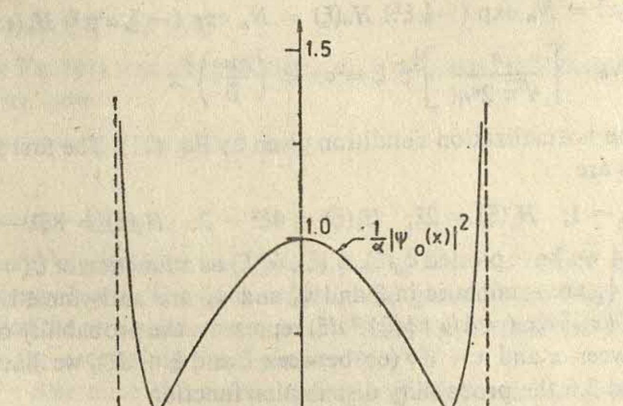

Fig. 3.5 The probability distribution function $|\psi_0(\xi)|^2$ for the ground state of the oscillator and the corresponding classical distribution (Eq. 117). (After Pauling and Wilson, 1935; used with permission.)

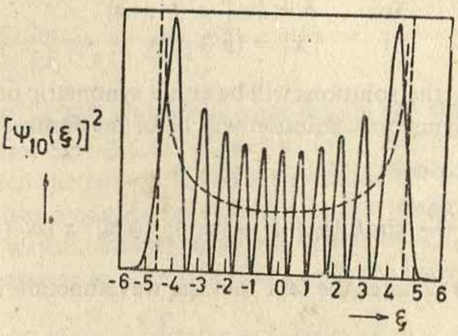

Fig. 3.6 The probability distribution function $|\psi_{10}(\xi)|^2$ for the $n = 10$ state of the oscillator. The dashed curve represents the corresponding classical distribution (Eq. 117). Notice that the average of the quantum mechanical result closely resembles the classical result [After Pauling and Wilson, 1935; used with permission].

fluctuations) there is a general agreement between the classical and quantum mechanical result; this is consistent with the correspondence principle.

3.6.4 The Double Well Potential

We next consider the double well potential shown in Fig. 3.7. A study of such a potential helps us to understand the formation of energy bands in a solid (see also Problem 4.4). Also the evolution of a wave packet with time (for a particle in a double well potential) gives very interesting results. The potential energy distribution is of the form (see Fig. 3.7)

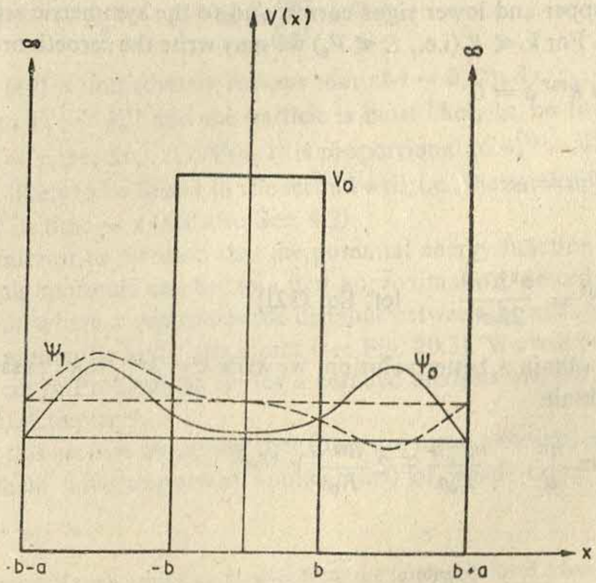

Fig. 3.7 The double well potential and qualitative variation of the lowest symmetric (solid curve) and the lowest antisymmetric (dashed curve) eigenfunctions.

$$V(x) = \begin{cases} V_0 & \text{for} \quad 0 < |x| < b \\ 0 & \text{for} \quad b < |x| < (b+a) \\ \infty & \text{at} \quad |x| = (b+a) \end{cases} \tag{76}$$

Since $V(-x) = V(x)$, the solutions will be either symmetric or antisymmetric in x. For $E < V_0$, the symmetric solution will be of the form

$$\begin{aligned} \psi_s(x) &= A_s \cosh Kx; \qquad 0 \leqslant |x| \leqslant b & (77) \\ &= \frac{A_s \cosh Kb}{\sin kb} \sin k\,(b + a - |x|); \quad b \leqslant |x| \leqslant (b+a) \end{aligned}$$

where the subscript s denotes the fact that the wavefunction is symmetric in x and

$$K = \left[\frac{2\mu}{\hbar^2}\left(V_0 - E\right)\right]^{\frac{1}{2}}, \quad k = \left[\frac{2\mu E}{\hbar^2}\right]^{\frac{1}{2}} \tag{78}$$

The constants in Eq. (77) are chosen such that $\psi_s(x)$ is continuous at $|x| = b$. Continuity of $d\psi/dx$ at $x = b$ gives

$$\begin{aligned} \tan ka &= -\frac{k}{K} \coth Kb = -\frac{k}{K}\,\frac{e^{Kb} + e^{-Kb}}{e^{Kb} - e^{-Kb}} \\ &\simeq -\frac{k}{K} - \frac{2k}{K}\, e^{-2Kb} \quad \text{(symmetric)} & (79) \end{aligned}$$

for $Kb \gg 1$. Similarly, one can consider the antisymmetric case. The eigenvalue equation can be combined to write it in the form

$$\tan ka \approx -\frac{k}{K} \mp \frac{2k}{K}\, e^{-2Kb} \tag{80}$$

where the upper and lower signs correspond to the symmetric and antisymmetric solution. For $k \ll K$ (i.e., $E \ll V_0$) we may write the zeroeth order solution as

$$\tan k^{(0)} a = 0$$

or

$$k^{(0)} a = n\pi \tag{81}$$

giving

$$E_n^{(0)} = \frac{\pi^2 \hbar^2 n^2}{2\mu a^2} \qquad \text{[cf. Eq. (32)]} \tag{82}$$

In order to obtain a better solution, we write $k = k^{(0)} + k^{(1)}$; assume $k^{(1)}a$ to be small and obtain

$$k \approx \frac{n\pi}{a} - \frac{n\pi/a}{K_0 a} \mp 2\,\frac{n\pi/a}{K_0 a}\, e^{-2K_0 b} \tag{83}$$

or

$$E_n \approx E_n^{(0)} - \frac{2E_n^{(0)}}{K_0 a} \mp 4\,\frac{E_n^{(0)}}{K_0 a}\, e^{-2K_0 b} \tag{84}$$

where

$$K_0 = \left[\frac{2m}{\hbar^2} (V_0 - E_n^{(0)}) \right]^{1/2} \tag{85}$$

For $V_0 \to \infty$, $E_n \to E_n^{(0)}$ which represent the energy levels for an infinitely deep potential well (see Sec. 3.6.1). However, for a finite value of V_0, there is a coupling between the two wells and the levels split*.

Figure 3.7 gives a qualitative variation of the lowest symmetric and lowest antisymmetric wavefunctions; these we denote by $\psi_s^{(1)}(x)$ and $\psi_a^{(1)}(x)$ respectively. It is interesting to note that if at $t = 0$, the wavefunction is given by**

$$\Psi(x, t = 0) = \frac{1}{\sqrt{2}} \left[\psi_s^{(1)}(x) + \psi_a^{(1)}(x) \right] \tag{86}$$

then at a later time, Ψ will be of the form [see Eq. (11)]

$$\begin{aligned} \Psi(x, t) &= \frac{1}{\sqrt{2}} \left[\psi_s^{(1)}(x) \exp\left\{ -iE_s^{(1)} \frac{t}{\hbar} \right\} + \psi_a^{(1)}(x) \exp\left\{ -iE_a^{(1)} \frac{t}{\hbar} \right\} \right] \\ &= \frac{1}{\sqrt{2}} e^{-iE_s^{(1)} t/\hbar} \left[\psi_s^{(1)}(x) + \psi_a^{(1)}(x)\, e^{-i\pi t/\tau} \right] \end{aligned} \tag{87}$$

where

$$\tau = \frac{\hbar}{\pi \Delta E^{(1)}}$$

and

$$\Delta E^{(1)} = E_a^{(1)} - E_s^{(1)} \approx 8 \frac{E_n^{(0)}}{K_0 a} e^{-2K_0 b} \tag{88}$$

From Eq. (87) it immediately follows that at $t = 0, 2\tau, 4\tau, \ldots$, $\Psi(x, t)$ is proportional to $\psi_s^{(1)} + \psi_a^{(1)}$ and the particle is most likely to be found in the first well. At $t = \tau, 3\tau, 5\tau, \ldots$, $\Psi(x, t)$ is proportional to $\psi_s^{(1)} - \psi_a^{(1)}$ and the particle is most likely to be found in the second well; i.e., the particle tunnels through the barrier in time $\sim \tau$ (see also Sec. 4.3).

It is of interest to mention that the potential energy function associated with the ammonia molecule can be, to a first approximation, described by a double well function where x represents the distance between the nitrogen atom and the plane containing the hydrogen atoms (see Fig. 20.3). We will briefly discuss the consequences in Problem 20.11; for a detailed analysis one may look up Feynman (1964), Chapter 9.

We end this section by noting that there are many potential energy variations (most of them have important applications) of which exact solutions of the

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*If there were N such wells (see Problem 4.4) the levels will form a band comprising of N levels. These are the energy bands in a solid.

**The factor $1/\sqrt{2}$ normalises $\Psi(x, t = 0)$.

Schrödinger equation are known. Examples are

$$V(x) = V_0 \operatorname{sech}^2 x/a \tag{89}$$

$$V(x) = \frac{V_1}{\cos^2 x/a} + \frac{V_2}{\sin^2 x/a} \tag{90}$$

$$V(x) = V_0\left(1 + \tanh \frac{x}{a}\right) \tag{91}$$

$$V(x) = V_0 \cot^2 \frac{\pi x}{a} \tag{92}$$

$$V(x) = V_0\left(\frac{a}{x} - \frac{x}{a}\right)^2 \quad (x > 0) \tag{93}$$

$$\left.\begin{aligned} V(x) &= \alpha x \\ &\ \infty \end{aligned}\right\} \begin{aligned} x &> 0 \\ x &= 0 \end{aligned} \tag{94}$$

etc. Some of the solutions will be discussed in the following problems. For other solutions the reader is referred to Constantinescu and Magyari (1971), Flugge (1971), Goldman and Krivchenkov (1961), Kogan and Galitsky (1963) and other similar books. For potentials for which exact solutions are not known, one employs approximate methods like the perturbation method (see Chapter 11), the variation method (see Chapter 12), the WKB method (see Chapter 13), etc.

PROBLEMS

Problem 3.1

Using the one dimensional Schrödinger equation show that the energy eigenvalue cannot be less than the absolute minimum of $V(x)$.

Problem 3.2

In order to determine the boundary condition of $V(x)$ going to infinity at a particular value of x (say $x = 0$), we consider the following limiting process: assume $V(x) = 0$ for $x < 0$ and $V(x) = V_0$ for $x > 0$; in the limit of $V_0 \to \infty$ show that ψ vanishes in the region $x > 0$.

Problem 3.3

Let $\phi_1, \phi_2, \ldots \phi_g$ represent a set of linearly independent eigenfunctions corresponding to a degenerate state. Construct appropriate linear combinations so that the wavefunctions form an orthonormal set.

Problem 3.4

Discuss the eigenvalues and eigenfunctions of the matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

Show that the vectors

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

belong to the degenerate state but do not form an orthonormal set. Use the results of the previous problem to obtain an orthonormal set.

Problem 3.5

Obtain the eigenvalues and (normalized) eigenvectors of the Hermitian matrix

$$\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

show that the eigenvectors are orthogonal to each other and that any vector like $\binom{a}{b}$ can be written as a linear combination of the eigenvectors.

Problem 3.6

For the one-dimensional potential well (Fig. 3.2), derive the transcendental equations determining the discrete eigenvalues [i.e., Eqs. (45) and (46)] without making the assumption that the wavefunctions have to be symmetric and antisymmetric functions of x.

Problem 3.7

Use the normalization condition to determine the values of A and B in Eq.(40).

Problem 3.8

For a linear harmonic oscillator prove that the expectation value of the potential energy in the nth state is given by

$$\langle V \rangle_n = \frac{1}{2}\left(n + \frac{1}{2}\right)\hbar\omega = \tfrac{1}{2} E_n \tag{95}$$

Further, the uncertainty product is given by (see also Sec. 8.9.1)

$$\Delta x \, \Delta p = \left(n + \frac{1}{2}\right)\hbar \tag{96}$$

Problem 3.9

Show that the quantum mechanical expression for the probability of finding the oscillator between x and $x + dx$ agrees with the classical expression for large quantum number n. [*Hint*: For large n, use the asymptotic forms of the Hermite polynomials—see Appendix G].

Problem 3.10

For the harmonic oscillator in the ground state calculate the probability of finding it beyond the classical limits.

Problem 3.11

For a particle inside an infinitely deep potential well (see Sec. 3.6.1) prove that

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{a^2}{12}\left(1 - \frac{6}{n^2\pi^2}\right) \tag{97}$$

PROBLEM 3.12

Show that the discrete energy levels for a particle experiencing a potential energy function

$$V(x) = -V_0 \operatorname{sech}^2 x/\sigma \tag{98}$$

are given by

$$E_n = -\frac{\hbar^2}{2m\sigma^2}\left[\frac{\nu}{2} - \left(n + \frac{1}{2}\right)\right]^2; \quad n = 0, 1, 2 \ldots \tag{99}$$

where

$$\nu = \left(\frac{8mV_0\sigma^2}{\hbar^2} + 1\right)^{\frac{1}{2}} \tag{100}$$

[*Hint*: Define

$$\xi = -\sinh^2\left(\frac{x}{\sigma}\right) \tag{101}$$

and

$$\psi(\xi) = [1 - \xi]^{-\frac{\nu-1}{2}} W(\xi) \tag{102}$$

Show that $W(\xi)$ satisfies the hypergeometric equation (see Appendix G). Apply the boundary condition that the wavefunction must vanish at $x = \pm\infty$.

PROBLEM 3.13

For a potential field of the form

$$V = V_0 \sec^2 (x/a) \tag{103}$$

use a method similar to that used in the previous problem to show that the energy eigenvalues are given by

$$E_n = \frac{V_0}{\nu(\nu - 1)}(\nu + n)^2; \quad n = 0, 1, 2 \ldots \tag{104}$$

where ν is the root (which is greater than 1) of the equation

$$\nu(\nu - 1) = \frac{2mV_0a^2}{\hbar^2} \tag{105}$$

[*Hint*: Define $\xi = \sin^2 x/a$ and $\psi(\xi) = (1 - \xi)^{\nu/2} F(\xi)$; show that $F(\xi)$ satisfies the hypergeometric equation (see Appendix G) and use the boundary condition that the wavefunction vanishes at $x = \pm\,\pi a/2$].

PROBLEM 3.14

Consider the bouncing of a particle over a horizontal plate of glass. Thus for $x > 0$, $V(x) = mgx$ and $\psi(x = 0) = 0$; the latter condition implying elastic reflection at $x = 0$. Introduce the new variable

$$\xi = \left(\frac{2m^2g}{\hbar^2}\right)^{1/3} x - \lambda; \quad \lambda = \left(\frac{\hbar^2}{2m^2g}\right)^{2/3}\frac{2mE}{\hbar^2} \tag{106}$$

and show that the wavefunction is of the form

$$\psi(\xi) \sim \frac{1}{3}\,|\,\xi\,|^{1/2}\,\{J_{-1/3}(\eta) + J_{1/3}(\eta)\} \qquad \text{for } \xi < 0$$

where $\eta = \frac{2}{3}\,|\,\xi\,|^{3/2}$. Applying the boundary condition at $x = 0$, show that for $n \gg 1$, the energy eigenvalues are determined by the following equation

$$E_n \approx \left(\frac{\hbar^2}{2m^2 g}\right)^{-2/3} \frac{\hbar^2}{2m}\left\{\frac{3\pi}{4}\left(2n - \frac{1}{2}\right)\right\}^{2/3} \tag{107}$$

[*Hint*: Use the asymptotic forms of Bessel functions; see Appendix H.]

PROBLEM 3.15

Solve the Schrödinger equation for the double oscillator for which the potential field is of the form

$$V(x) = \frac{1}{2} m\omega^2\,(\,|\,x\,| - a)^2 \tag{108}$$

Compare the results with those obtained in Sec. 3.6.3.

SOLUTIONS

SOLUTION 3.1

We write the Schrödinger equation in the form

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\Big[V(x) - E\Big]\psi$$

If $V(x) > E$ for all values of x then ψ'' has the same sign as ψ everywhere. Thus if ψ is positive at some value of x then ψ'' will also be positive. Hence if $\psi' > 0$ then $\psi \to \infty$ as $x \to \infty$ and if $\psi' < 0$ then $\psi \to \infty$ as $x \to -\infty$. As such we must have some value of x for which $E = V(x)$.

SOLUTION 3.2

Since $V(x) = 0$ for $x < 0$ and $V = V_0$ for $x > 0$ the solution of the Schrödinger equation is

$$\begin{aligned} \psi(x) &= A \sin kx + B \cos kx && \text{for } x < 0 \\ &= Ce^{-\kappa x} && \text{for } x > 0 \end{aligned}$$

where $k = (2mE/\hbar^2)^{1/2}$ and $\kappa = [2m(V_0 - E)/\hbar^2]^{1/2}$; we have assumed $V_0 > E$ and rejected the solution $e^{\kappa x}$ which goes to ∞ as $x \to \infty$. Continuity of ψ and $d\psi/dx$ at $x = 0$ gives

$$\begin{aligned} C &= B \\ C &= -\frac{k}{\kappa}A = -\left(\frac{1}{\frac{V_0}{E} - 1}\right)^{\frac{1}{2}} A \end{aligned}$$

Thus as $V_0 \to \infty, C \to 0$ (and hence $B \to 0$) implying that $\psi = 0$ for $x \geqslant 0$.

Solution 3.3

Let

$$v_1 = \phi_1, \quad \psi_1 = \frac{v_1}{l_1}, \quad l_1 = \left[\int v_1^* \, v_1 \, dx\right]^{\frac{1}{2}} \tag{109}$$

l_1 is known as the length of the vector v_1 (see Sec. 7.1). We next define

$$v_2 = \phi_2 - c_{21}\psi_1, \quad \psi_2 = \frac{v_2}{l_2}, \quad l_2 = \left[\int v_2^* \, v_2 \, dx\right]^{\frac{1}{2}} \tag{110}$$

c_{21} is such that v_2 is orthogonal to ψ_1

$$0 = \int v_2 \, \psi_1^* \, dx = \int \phi_2 \, \psi_1^* \, dx - c_{21}$$

or

$$c_{21} = \int \phi_2 \psi_1^* \, dx$$

Similarly

$$v_3 = \phi_3 - c_{31}\,\psi_1 - c_{32}\,\psi_2, \; \psi_3 = \frac{v_3}{l_3}, \; l_3 = \left[\int v_3^* \, v_3 \, dx\right]^{1/2} \tag{111}$$

$$c_{31} = \int \psi_1^* \, \phi_3 \, dx \quad \text{and } c_{32} = \int \psi_2^* \, \phi_3 \, dx \tag{112}$$

are such that v_3 is orthogonal to ψ_1 and ψ_2. In general

$$\begin{aligned} v_{n+1} &= \phi_{n+1} - \sum_{m=1}^{n} \left[\int \psi_m^* \, \phi_{n+1} \, dx\right] \psi_m, \\ \psi_{n+1} &= v_{n+1}/l_{n+1}, \; l_{n+1} = \left[\int v_{n+1}^* \, v_{n+1} \, dx\right]^{\frac{1}{2}} \end{aligned} \tag{113}$$

Thus $v_1, v_2, \ldots.$ form an orthonormal set. This is known as Schmidt's orthogonalization procedure.

Solution 3.4

We choose

$$\psi_1 = v_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$c_{21} = (\; 1 \; 1 \; 0 \;) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 1$$

$$v_2 = \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} - \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \psi_2$$

ψ_1 and ψ_2 form an orthonormal set and correspond to the degenerate eigenvalue.

It may be mentioned that

$$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\\0\end{pmatrix} \quad \text{and} \quad \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\\0\end{pmatrix}$$

also form an orthonormal set. Thus there can be an infinite number of orthonormal sets.

SOLUTION 3.6

The wavefunction would be given by

$$\psi = \begin{cases} A \exp(\kappa x) & \text{for } x < -a/2 \\ B \sin kx + C \cos kx & \text{for } -a/2 < x < a/2 \\ D \exp(-\kappa x) & \text{for } x > a/2 \end{cases} \tag{114}$$

continuity of ψ and $d\psi/dx$ at $x = \pm a/2$ will give us four equations from which we may obtain

$$2B \sin \eta = (D - A)\, e^{-\xi}, \quad 2kB \cos \eta = \kappa(-D + A)\, e^{-\xi} \tag{115}$$

$$2C \cos \eta = (D + A)\, e^{-\xi}, \quad 2kC \sin \eta = \kappa(D + A)\, e^{-\xi} \tag{116}$$

where $\eta = ka/2$ and $\xi = \kappa a/2$. From this we immediately see that
either $B = 0$ and $D = A$ (the symmetric solution) and one obtains Eq. (45),
or $C = 0$ and $D = -A$ (the antisymmetric solution) and one obtains Eq. (46).

SOLUTION 3.7

For the symmetric mode

$$B = \left[\exp\left(\frac{\kappa a}{2}\right)\cos\frac{ka}{2}\right]A$$

and the normalization condition gives us

$$|A| = \left(\frac{2}{a}\right)^{\frac{1}{2}}\left[1 + \frac{\sin ka}{ka} + \frac{2\cos^2(ka/2)}{\kappa a}\right]^{-1/2}$$

SOLUTION 3.8

Using the generating function of Hermite polynomials (see Appendix G) it can be shown that

$$\int_{-\infty}^{\infty} \psi_n^*(x)\, x^2\, \psi_n(x)\, dx = |N_n|^2 \int_{-\infty}^{\infty} H_n^2(\alpha x)\, e^{-\alpha^2 x^2}\, dx = \frac{2n+1}{\alpha^2}$$

Therefore

$$\langle V \rangle_n = \int_{-\infty}^{\infty} \psi_n^*(x)\, \frac{1}{2}\, m\omega^2 x^2\, \psi_n(x)\, dx$$

$$= \frac{1}{2}\left(n + \frac{1}{2}\right)\hbar\omega = \frac{1}{2}E_n$$

Further

$$\left\langle \frac{p^2}{2m} \right\rangle_n = \langle H \rangle_n - \langle V \rangle_n = \frac{1}{2} E_n$$

Now

$$\langle x \rangle_n = 0 \qquad \text{and} \quad \langle p \rangle_n = 0$$

because in both the cases the integrand is an odd function of x. Thus

$$\Delta x \, \Delta p = [\langle x^2 \rangle \langle p^2 \rangle]^{1/2} = (n + \tfrac{1}{2}) \hbar$$

Solution 3.9

Classically, the probability of finding the oscillator between x and $x + dx$ is given by

$$P(x) \, dx = \frac{(dx/v)}{T} = \frac{dx}{\pi(a^2 - x^2)^{1/2}} \tag{117}$$

where a is the amplitude of the oscillation. Notice that $\int_{-a}^{a} P(x) \, dx = 1$· Quantum mechanically

$$P(x) = |\psi_n|^2 = \frac{\alpha}{2^n n! \sqrt{\pi}} \exp(-\xi^2) \, H_n^2(\xi)$$

$$\sim \frac{2\alpha}{\pi \sqrt{2n - \xi^2}} \cos^2 \left[\left(2n + \frac{1}{2} \right) \frac{\xi}{\sqrt{2n}} - \frac{n\pi}{2} \right]$$

where $\xi = \alpha x = \sqrt{\dfrac{m\omega}{\hbar}} \, x$ and use has been made of the Stirling's formula $[n! \simeq \sqrt{2n\pi} \, (n/e)^n]$ and the asymptotic expression (valid for large n)

$$H_n(\xi) \sim \frac{2^{n+1} \left(\dfrac{n}{2e} \right)^{n/2}}{\sqrt{2} \cos \beta} \exp(n\beta^2) \cos \left[\left(2n + \frac{1}{2} \right) \beta - \frac{n\pi}{2} \right] \tag{119}$$

β is the smallest positive angle whose sine is $\xi/\sqrt{2n}$. The average of the factor $\cos^2 [\cdots\cdot]$ over many periods is $\frac{1}{2}$ and since the total energy of the oscillator is $\frac{1}{2} m\omega^2 a^2$, we have

$$a = \left(\frac{2E}{m\omega^2} \right)^{\frac{1}{2}} = \left(\frac{\sqrt{2n + 1}}{\alpha} \right) \sim \left(\frac{\sqrt{2n}}{\alpha} \right)$$

we obtain

$$P(x) = \frac{1}{\pi \sqrt{a^2 - x^2}} \tag{120}$$

Solution 3.10

The required probability is

$$2 \int_{a}^{\infty} |\psi_0(x)|^2 \, dx \simeq 0.16$$

SOLUTION 3.12

If we make the substitutions defined through Eqs. (101) and (102), we would find that $W(\xi)$ satisfies the equation

$$\xi(1-\xi)\,\frac{d^2W}{d\xi^2}+\left[c-\left(a+b+1\right)\xi\right]\frac{dW}{d\xi}-a\,b\,W(\xi)=0 \qquad (121)$$

where

$$\left.\begin{aligned} &a=\Delta-\tfrac{1}{2}(\nu-1), \quad b=-\Delta-\tfrac{1}{2}(\nu-1) \\ &c=\tfrac{1}{2}, \ \Delta=\left(-\frac{mEa^2}{2\hbar^2}\right)^{1/2} \end{aligned}\right\} \qquad (122)$$

Equation (121) is the hypergeometric equation (see Appendix G) the solutions of which are $F(a, b, c; \xi)$ and $\xi^{1-c}F(a+1-c, b+1-c, 2-c; \xi)$. For the wavefunction to vanish as $x \to \pm\infty$ (i.e., $\xi \to -\infty$), $W(\xi)$ should be a polynomial. For the first solution this can happen if a or b is a negative integer but for b equal to a negative integer, the wavefunction increases exponentially; thus a should be a negative integer. Similarly, for the other solution, $a+1-c$ should be a negative integer. Combining the two equations we get Eq. (99).

SOLUTION 3.15

We introduce the variables

$$\xi=\left(\frac{2m\omega}{\hbar}\right)^{1/2}(x-a) \qquad \text{for} \quad x>0 \qquad (123)$$

and

$$\zeta=\left(\frac{2m\omega}{\hbar}\right)^{1/2}(x+a) \qquad \text{for} \quad x<0 \qquad (124)$$

The Schrödinger equation becomes

$$\frac{d^2\psi}{d\xi^2}+\left(\nu+\frac{1}{2}-\frac{\xi^2}{4}\right)\psi=0 \qquad \text{for} \quad x>0 \qquad (125)$$

and

$$\frac{d^2\psi}{d\zeta^2}+\left(\nu+\frac{1}{2}-\frac{\zeta^2}{4}\right)\psi=0 \qquad \text{for} \quad x<0 \qquad (126)$$

where

$$\nu=\frac{1}{2}(\mathcal{E}-1), \quad \mathcal{E}=\frac{2E}{\hbar\omega} \qquad (127)$$

The boundary conditions for solving Eqs. (125) and (126) are now, $\psi \to 0$ as $\xi \to \infty$ and $\zeta \to -\infty$. Observe that for $a=0$ Eqs. (125) and (126) become equivalent to the harmonic oscillator equation and ν will then be 0, 1, 2, . . .

The solution of Eq. (125) vanishing for $\xi \to \infty$ is the parabolic cylinder function* $D_\nu(\xi)$ which is related to the confluent hypergeometric function (see

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*See, e.g., Magnus, Oberhettinger and Soni (1966), p. 323.

Appendix G) through the following relation:

$$D_\nu(\xi) = 2^{\nu/2}\, e^{-\xi^2/4}\left[\frac{\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(\frac{1-\nu}{2}\right)}\, {}_1F_1\left(-\frac{\nu}{2}\,;\,\frac{1}{2}\,;\,\frac{\xi^2}{2}\right) + \frac{\xi}{\sqrt{2}}\,\frac{\Gamma\left(-\frac{1}{2}\right)}{\Gamma\left(-\frac{\nu}{2}\right)}\, {}_1F_1\left(\frac{1-\nu}{2}\,;\,\frac{3}{2}\,;\,\frac{\xi^2}{2}\right)\right] \tag{128}$$

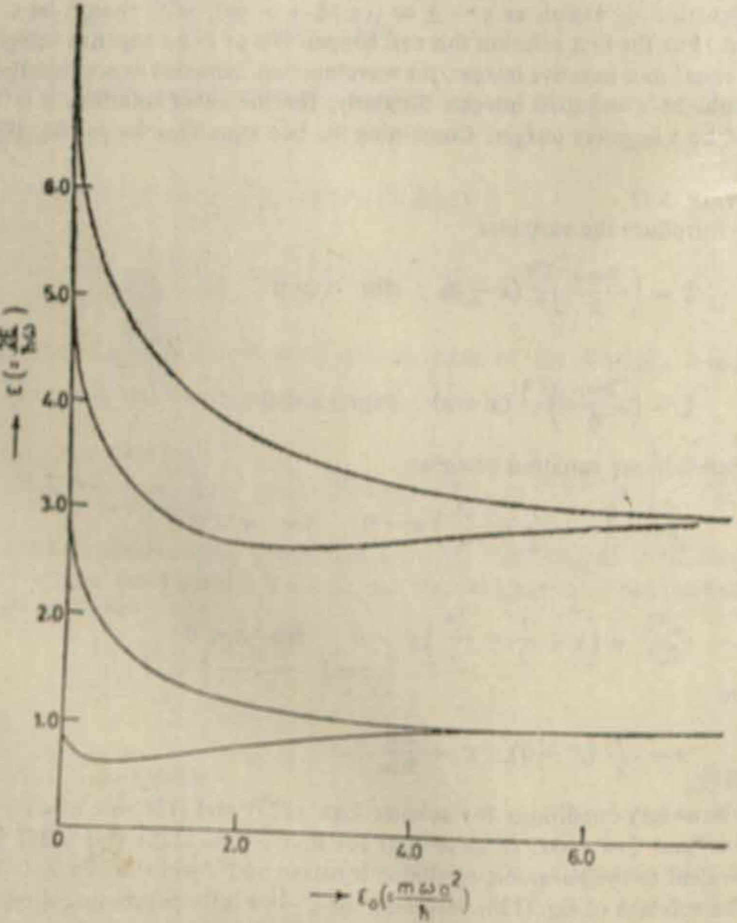

Fig. 3.8 The variation of $2E/\hbar\omega$ with $\mathcal{E}_0\ (= m\omega a^2/\hbar)$. Notice that as $a \to \infty$, the energy eigenvalues correspond to two independent harmonic oscillators.

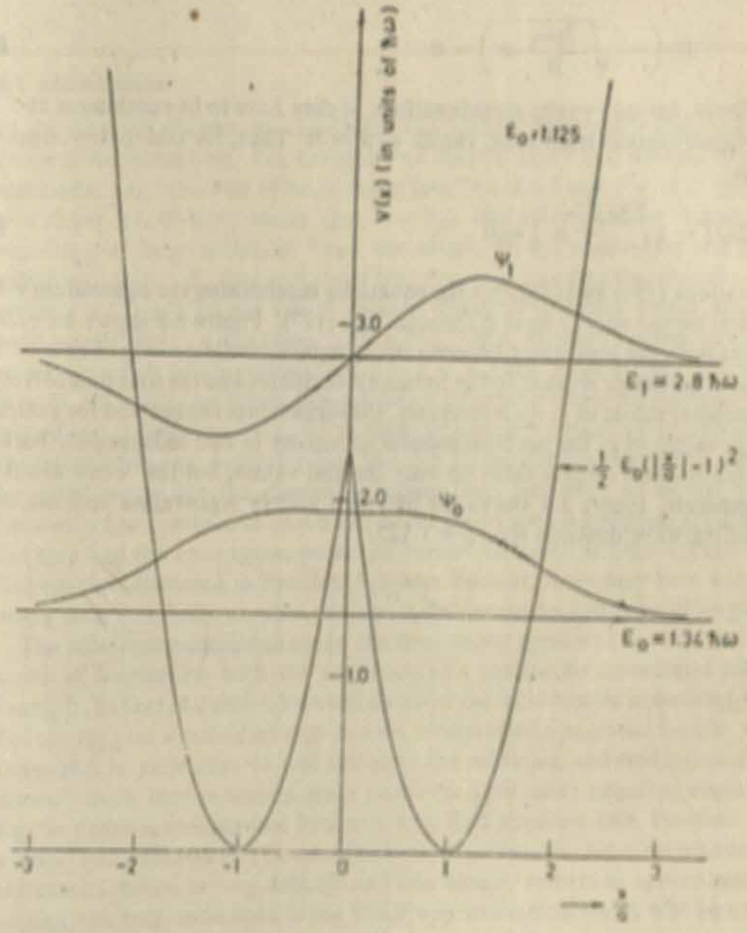

Fig. 3.9 Potential energy variation for the double oscillator (see Eq. 108) and the corresponding first two energy levels and wavefunctions. The calculations correspond to $\mathcal{E}_0 =$ 1.125.

Since

$$\underset{\zeta \to \infty}{\mathrm{Lt}} \; D_\nu(\zeta) = 0 \tag{129}$$

we must choose the solution $D_\nu(\zeta)$ for $x > 0$ and $D_\nu(-\zeta)$ for $x < 0$. (Thus ϕ would tend to zero as $x \to \pm \infty$). Further, since the potential is symmetric about $x = 0$, the solutions can be broken into even parity and odd parity wavefunctions. We now apply the condition of continuity of ψ and $d\psi/dx$ at $x = 0$. For even parity eigenfunctions, if the slope has to be continuous at $x = 0$, the slope must be zero, i.e., for even parity eigenfunctions

$$D'_\nu(\zeta)\big|_{x=0} = 0 = D'_\nu(-\zeta)\big|_{x=0} \tag{130}$$

giving

$$D'_\nu\left(-\sqrt{\frac{2m\omega}{\hbar}}\,a\right)=0 \tag{131}$$

Similarly, for odd parity eigenfunctions, if they have to be continuous at $x = 0$, the eigenfunction itself must vanish at $x = 0$. Thus, for odd parity eigenfunctions

$$D_\nu\left(-\sqrt{\frac{2m\omega}{\hbar}}\,a\right)=0 \tag{132}$$

Equations (131) and (132) are the equations determining the eigenvalues ν which determine the energy level E through Eq. (127). Figure 3.8 shows how $2E/\hbar\omega$ varies with the separation between the harmonic oscillator wells. For $a = 0$, the double oscillator reduces to the harmonic oscillator and the solutions correspond to integral values of ν. As a increases, the eigenvalues change and for sufficiently large values of a, the problem reduces essentially to two independent harmonic oscillators and ν again takes on only integral values, but the levels are doubly degenerate. Figure 3.9 shows the first two energy eigenvalues and the corresponding wavefunctions for $\mathcal{E}_0 = 1.125$.

CHAPTER FOUR

One Dimensional Barrier Transmission Problems

4.1 Introduction

In the previous chapter we considered the bound states corresponding to one dimensional potentials. For example, we showed that for a particle in a one dimensional potential well of finite depth (see Sec. 3.6.2 and Fig. 3.2) there exist a number of discrete states (for $E < V_0$), the corresponding wavefunctions vanishing at large distances from the origin. In this chapter we will consider solutions for $E > V_0$ and will show that the corresponding wavefunctions in the region $|x| > a/2$ do not vanish at large distances from the origin and E can have any arbitrary value (greater than V_0). Thus, for such a potential well there exists a number of discrete states (with $E < V_0$) and a continuum of states for $E > V_0$. It may be mentioned that there are situations where the continuous spectrum does not exist at all; e.g., for the infinitely deep potential well (see Sec. 3.6.1), the linear harmonic oscillator (see Sec. 3.6.3), etc. On the other hand, there may be situations where the discrete spectrum may not exist at all and one may have only the continuous spectrum; examples of such a situation are the potential step and the rectangular potential barrier discussed in Secs. 4.2 and 4.3, the free particle discussed in Problem 8.2, etc. Further, there may be a continuum along with an infinite number of discrete states as in the hydrogen atom problem.

The solutions corresponding to the continuous spectrum are of great importance in connection with the scattering of a particle by a potential field. For example, in Secs. 4.2 and 4.3 we will consider the incidence of a particle (of specified energy) on a potential step and on a rectangular potential barrier respectively and in each case we will calculate the reflection and transmission coefficients.* Such barrier transmission problems have many practical applications, e.g., in Esaki tunnelling (see Problem 4.8), field emission (see Problem 13.10), α-decay (see Problem 13.17), etc. However, unfortunately for most practical cases the exact solution is very difficult and one usually resorts to approximate techniques; one such technique is the WKB approximation which will be discussed in Chapter 13 along with some practical applications.

4.2 The Potential Step

We first consider a potential step (see Fig. 4.1) for which

$$\begin{aligned} V(x) &= 0 \quad \text{for} \quad x < 0 \\ &= V_0 \quad \text{for} \quad x \geqslant 0 \end{aligned} \tag{1}$$

We consider the incidence of a particle (of energy E) from the left on the

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*In the corresponding three dimensional situation, the scattering occurs into a solid angle $d\Omega$; see Chapter 19.

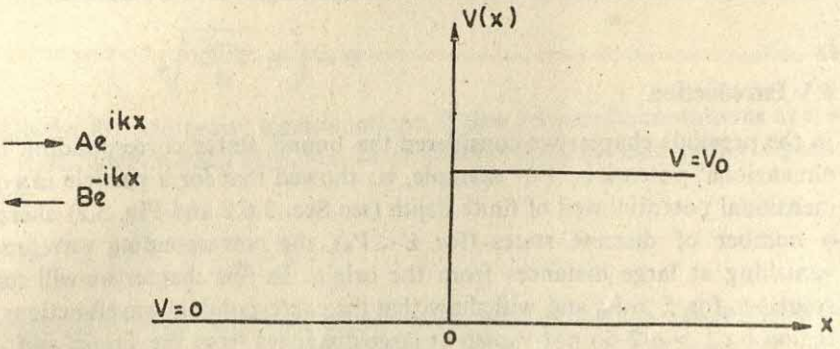

Fig. 4.1 The potential step.

barrier. Classically, if $E > V_0$, the particle penetrates the barrier and keeps on moving (with reduced kinetic energy) in the positive x direction; on the other hand, if $E < V_0$ the particle is reflected back at $x = 0$ because the particle does not have sufficient energy to be in the region $x > 0$. Quantum mechanically, we will show that for $E > V_0$, the particle may undergo reflection and for $E < V_0$, although the reflection coefficient is unity, the wavefunction is non-zero in the region $x > 0$ implying that there is a finite probability of finding the particle in the region $x > 0$.

We will first discuss the case $E > V_0$. The Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \text{for} \quad x < 0$$

and (2)

$$\frac{d^2\psi}{dx^2} + k_1^2\psi = 0 \qquad \text{for} \quad x > 0$$

where

$$k = [2mE/\hbar^2]^{1/2} \quad \text{and} \quad k_1 = [2m(E - V_0)/\hbar^2]^{1/2} \tag{3}$$

The solutions are

$$\begin{aligned} \psi &= Ae^{ikx} + Be^{-ikx} \qquad &\text{for} \quad x < 0 \\ &= Ce^{ik_1x} + De^{-ik_1x} \qquad &\text{for} \quad x > 0 \end{aligned} \tag{4}$$

If we multiply the wavefunctions by the time-dependent factor $\exp(-iEt/\hbar)$ we can interpret the terms Ae^{ikx} and Ce^{ik_1x} as waves propagating in the $+x$ direction and the terms Be^{-ikx} and De^{-ik_1x} as waves propagating in the $-x$ direction. Since we are considering the incidence of a particle from the left on the barrier at $x = 0$, there cannot be a wave propagating in the $-x$ direction in region $x > 0$ and hence we must put $D = 0$. Continuity of ψ and $d\psi/dx$ at $x = 0$ gives us

$$A + B = C$$

and

$$ik(A - B) = ik_1C$$

from which we readily obtain

$$B = \frac{k - k_1}{k + k_1} A \tag{5}$$

$$C = \frac{2k}{k + k_1} A \tag{6}$$

Now, the current density is given by [see Eq. (36) of Chapter 2]

$$J = \text{Re}\left[\psi^* \frac{\hbar}{im} \frac{\partial \psi}{\partial x}\right] \tag{7}$$

The current densities associated with the wavefunctions Ae^{ikx}, Be^{-ikx} and Ce^{ik_1x} represent the incident current, reflected current and transmitted current respectively; these are given by

$$J\text{inc} = \frac{\hbar k}{m} |A|^2 \tag{8}$$

$$J\text{ref} = \frac{\hbar k}{m} |B|^2 \tag{9}$$

and

$$J\text{tr} = \frac{\hbar k_1}{m} |C|^2 \tag{10}$$

Thus the reflection and transmission coefficients are given by

$$R = \frac{J\text{ref}}{J\text{inc}} = \frac{|B|^2}{|A|^2} = \frac{(k - k_1)^2}{(k + k_1)^2} \tag{11}$$

and

$$T = \frac{J\text{tr}}{J\text{inc}} = \frac{k_1 |C|^2}{k\ |A|^2} = \frac{4kk_1}{(k + k_1)^2} \tag{12}$$

It is easy to see that $R + T = 1$ as it indeed should be.

For $E < V_0$, the analysis remains similar except that k_1 has to be replaced by $i\kappa$.

$$k_1 \to i\kappa = i\left[\frac{2m}{\hbar^2}\left(V_0 - E\right)\right]^{1/2} \tag{13}$$

In the region $x > 0$ we now have solutions $Ce^{-\kappa x}$ and $De^{\kappa x}$. We have to reject the latter because it increases indefinitely with x. Continuity of ψ and $d\psi/dx$ leads to

$$B = \frac{k - i\kappa}{k + i\kappa} A = e^{-2i\alpha} A \tag{14}$$

where

$$\tan \alpha = \kappa/k \tag{15}$$

Equation (14) tells us that there is a phase change on reflection but the amplitude of the reflected wave is the same as that of the incident wave. In the region

$x > 0$, since the wavefunction is now real, the transmitted current vanishes and one has

$$R = 1 \quad \text{and} \quad T = 0 \tag{16}$$

It may be noted that although the transmission coefficient vanishes, the wavefunction is not zero in the region $x > 0$, i.e., there is a finite probability of finding the particle in the 'classically-forbidden' region. However, in order to observe the particle in the region $x > 0$, $\Delta x \sim 1/\kappa$ (see Problem 4.7) and therefore the uncertainty in the momentum should be given by

$$\Delta p \gtrsim \frac{\hbar}{\Delta x} \sim \hbar\kappa \sim \sqrt{2m(V_0 - E)} \tag{17}$$

The uncertainty in the kinetic energy will be $\sim (\Delta p)^2/2m \sim (V_0 - E)$ which should be sufficient to raise it to the classically allowed region. Thus, if we try to observe the particle in the region $x > 0$ we necessarily impart so much of kinetic energy to it that the total energy is greater than V_0.

In order to get a better physical insight, we should consider the reflection (and transmission) of a wave packet. This is discussed in Sec. 4.4 (see also Problem 4.6).

4.3 The Rectangular Potential Barrier

We next consider a potential barrier of the type shown in Fig. 4.2. Classically, for a particle of energy E incident on the barrier, if $E < V_0$ the particle gets reflected by the barrier and if $E > V_0$ the particle gets transmitted through the barrier. We will see that according to quantum mechanics, even for $E < V_0$ there is a finite probability of the particle *tunnelling* through the barrier. This is entirely a quantum mechanical effect and field emission of electrons (see Problem 13.10), emission of α particles from the nucleus (see Problem 13.17), etc. are examples of this tunnelling phenomenon. Further, for $E > V_0$, there may be a finite probability for reflection.

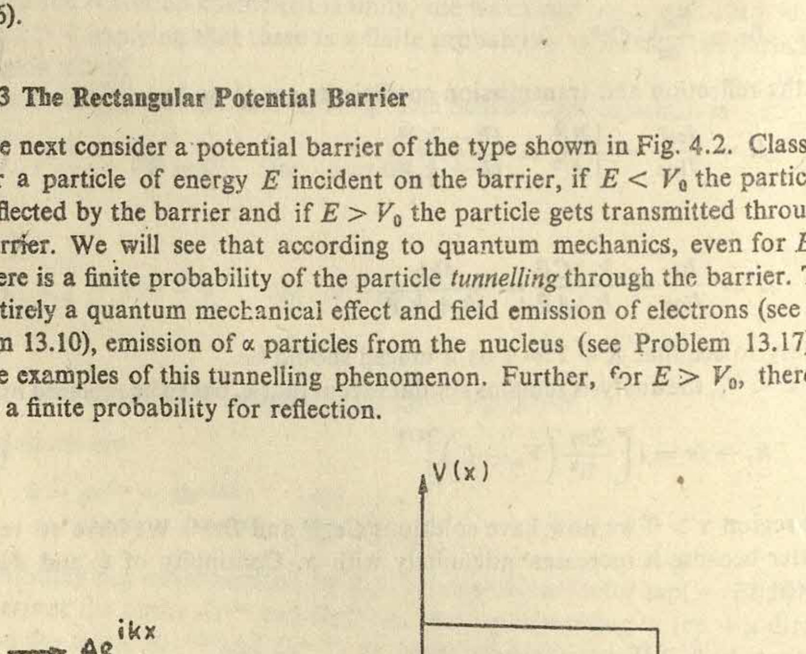

Fig. 4.2 A rectangular potential barrier.

We first consider $E < V_0$. For such a case the solutions of the Schrödinger equation in the three regions are given by

$$\begin{aligned} \psi &= Ae^{ikx} + Be^{-ikx} \qquad & x < 0 \\ &= Ce^{\kappa x} + De^{-\kappa x} \qquad & 0 < x < a \\ &= Fe^{ikx} + Ge^{-ikx} \qquad & x > a \end{aligned} \tag{18}$$

where

$$k = \left(\frac{2mE}{\hbar^2}\right)^{1/2} \quad \text{and } \kappa = \left(\frac{2m(V_0 - E)}{\hbar^2}\right)^{1/2} \tag{19}$$

As in Sec. 4.2 we set $G = 0$ because there cannot be a wave propagating in the $-x$ direction in the region $x > a$. Continuity of ψ and $d\psi/dx$ at $x = 0$ and at $x = a$ give us

$$A + B = C + D$$

$$\frac{ik}{\kappa}(A - B) = C - D$$

Thus

$$C = \frac{1}{2}\left(1 + \frac{ik}{\kappa}\right)A + \frac{1}{2}\left(1 - \frac{ik}{\kappa}\right)B \tag{20}$$

and

$$D = \frac{1}{2}\left(1 - \frac{ik}{\kappa}\right)A + \frac{1}{2}\left(1 + \frac{ik}{\kappa}\right)B \tag{21}$$

Continuity conditions at $x = a$ give us

$$Ce^{\kappa a} + De^{-\kappa a} = Fe^{ika} \tag{22}$$

and

$$\kappa Ce^{\kappa a} - \kappa De^{-\kappa a} = ikFe^{ika} \tag{23}$$

Substituting for C and D in Eqs. (20) and (21), one can immediately get the ratios B/A and F/A :

$$\frac{B}{A} = \frac{(k^2 + \kappa^2)(1 - e^{2\kappa a})}{(k - i\kappa)^2 - (k + i\kappa)^2 e^{2\kappa a}} \tag{24}$$

$$\frac{F}{A} = \frac{(-i)\, 4k\kappa e^{-ika} e^{\kappa a}}{(k - i\kappa)^2 - (k + i\kappa)^2 e^{2\kappa a}} \tag{25}$$

which lead to the following expressions for the reflection and transmission coefficients

$$R = \frac{J\text{ref}}{J\text{inc}} = \frac{\frac{\hbar k}{m}|B|^2}{\frac{\hbar k}{m}|A|^2} = \left[1 + \frac{4\varepsilon(1 - \varepsilon)}{\sinh^2 \kappa a}\right]^{-1} \tag{26}$$

$$T = \frac{J\text{tran}}{J\text{inc}} = \frac{\frac{\hbar k}{m}|F|^2}{\frac{\hbar k}{m}|A|^2} = \left[1 + \frac{\sinh^2 \kappa a}{4\varepsilon(1 - \varepsilon)}\right]^{-1} \tag{27}$$

where $\varepsilon = E/V_0$. Notice that $R + T = 1$. Further, we may write

$$\kappa a = \alpha \sqrt{1 - \varepsilon} \tag{28}$$

where

$$\alpha = \left(\frac{2mV_0a^2}{\hbar^2} \right)^{1/2} \tag{29}$$

is a dimensionless variable characterising the potential. It may be noted that for $\kappa a \gg 1$

$$T \approx 16\varepsilon\,(1 - \varepsilon)\, e^{-2\kappa a} \tag{30}$$

For $E > V_0$, the analysis is very similar, excepting that, in the region $0 < x < a$, instead of the solutions $e^{\pm \kappa x}$ we will have solutions $e^{\pm ik_1x}$ where

$$k_1 = \left[\frac{2m(E - V_0)}{\hbar^2} \right]^{1/2} \tag{31}$$

Thus we have to replace κ by ik_1, everywhere. The final results are

$$R = \left[1 + \frac{4\varepsilon(\varepsilon - 1)}{\sin^2 k_1a} \right]^{-1} \tag{32}$$

$$T = \left[1 + \frac{\sin^2 k_1a}{4\varepsilon(\varepsilon - 1)} \right]^{-1} \tag{33}$$

Once again $R + T = 1$. In Fig. 4.3 we have plotted the variation of the transmission coefficient with $\varepsilon(= E/V_0)$ for $\alpha = 10.0$. It may be noticed that the

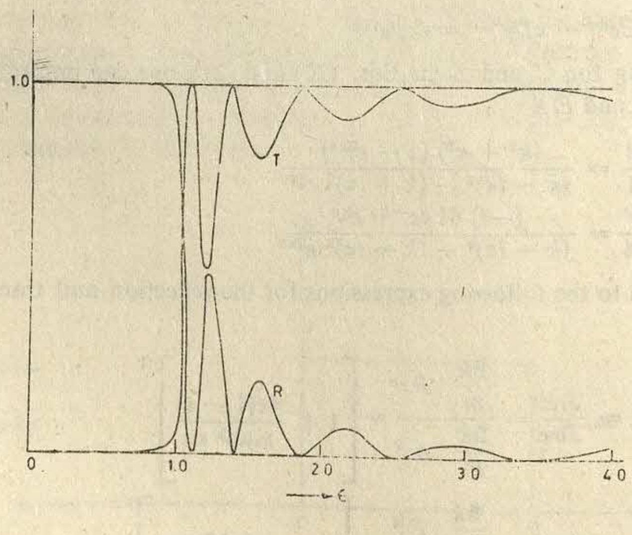

Fig. 4.3 The variation of the reflection and transmission coefficients with $\varepsilon = (E/V_0)$ for a rectangular potential barrier (see Fig. 4.2) with $\alpha = 10.0$.

transmission coefficient is unity for

$$k_1 a = \pi, 2\pi, \ldots . \tag{34}$$

or

$$a = \frac{\lambda_1}{2}, 2\left(\frac{\lambda_1}{2}\right), 3\left(\frac{\lambda_1}{2}\right), \ldots . \tag{35}$$

where $\lambda_1 = 2\pi/k_1$. Thus whenever the barrier width is a multiple of $\lambda_1/2$ perfect transmission occurs*. This is also observed for a potential well as discussed in Problem 4.1.

4.4 The Reflection and Transmission of a Wave Packet

In the analysis discussed in Secs. 4.2. and 4.3 we obtained expressions for the reflection and transmission coefficients by considering the time independent solutions of the Schrödinger equation. However, in order to get a better physical insight we consider the incidence of a wave packet on a potential barrier. For the sake of simplicity we consider the reflection of a wave packet by a potential step; similar analysis can be carried out for other potential barriers also.

We assume that the component waves, the superposition of which gives the wave packet, correspond to $E < V_0$ so that the solution in the region $x < 0$ is of the form [see Eqs. (4) and (5) with k_1 replaced by $i\kappa$]:

$$\begin{aligned}\psi &= A\left[e^{ikx} + \frac{k - i\kappa}{k + i\kappa}\, e^{-ikx}\right] \\ &= A\left[e^{ikx} + e^{-2i\alpha(k)}\, e^{-ikx}\right]\end{aligned} \tag{36}$$

where

$$\tan\alpha(k) = \frac{\kappa}{k} = \left(\frac{V_0 - E}{E}\right)^{1/2} = \left[\frac{\beta^2 - k^2}{k^2}\right]^{1/2} \tag{37}$$

$$\beta = \left[\frac{2mV_0}{\hbar^2}\right]^{1/2} \tag{38}$$

Thus a wave packet in the region $x < 0$ will be of the form

$$\begin{aligned}\Psi(x, t) &= \frac{1}{\sqrt{2\pi}} \int_0^{\beta} A(k)\left[e^{ikx} + e^{-2i\alpha(k)}\, e^{-ikx}\right] e^{-i\omega(k)t}\, dk \\ &= \frac{1}{\sqrt{2\pi}} \int_0^{\beta} |A(k)| \left[e^{i[kx - \omega(k)t + \phi(k)]} + e^{-i[kx + \omega(k)t + 2\alpha(k) - \phi(k)]}\right] dk\end{aligned} \tag{39}$$

where

$$A(k) = |A(k)|\, e^{i\phi(k)} \tag{40}$$

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*This is indeed similar to the interference pattern observed in a Fabry-Perot etalon (see, e.g., Ghatak, 1977).

and

$$\omega(k) = \frac{E(k)}{\hbar} = \frac{\hbar k^2}{2m} \tag{41}$$

[see Eq. (3)]. It should be mentioned that since $E < V_0$, k is less than β and $\theta(k)$ is real*. Now, Eq. (39) can be written in the form

$$\Psi(x, t) = \Psi_{inc}(x, t) + \Psi_{ref}(x, t) \tag{42}$$

where

$$\Psi_{inc}(x, t) = \frac{1}{\sqrt{2\pi}} \int_0^\beta |A(k)| \exp [i(kx - \omega(k)t + \phi(k))] \, dk \tag{43}$$

and

$$\Psi_{ref}(x, t) = \frac{1}{\sqrt{2\pi}} \int_0^\beta |A(k)| \exp [-i(kx + \omega(k)t + 2\theta(k) - \phi(k))] dk \tag{44}$$

represent the packets describing the incident and reflected waves respectively. As in Sec. 2.7 we assume $|A(k)|$ to be sharply peaked around $k = k_0$; thus, the centre of the wave packet associated with the incident and reflected waves would be given by [see Eqs. (76) and (79) of Chapter 2]

$$x_c^{inc}(t) = -a + v_g t \tag{45}$$

$$x_c^{ref}(t) = a - v_g t + \tau \tag{46}$$

where

$$a = \left.\frac{\partial \phi}{\partial k}\right|_{k=k_0} \tag{47}$$

$$v_g = \left.\frac{d\omega}{dk}\right|_{k=k_0} = \frac{\hbar k_0}{m} \tag{48}$$

and

$$\tau = -\left.\frac{2 d\theta(k)}{dk}\right|_{k=k_0} = \frac{2}{(\beta^2 - k_0^2)^{1/2}} \tag{49}$$

represents the time delay** introduced during reflection of the packet. Obviously, both $x_c^{inc}(t)$ and $x_c^{ref}(t)$ should be negative because $\Psi(x, t)$ as given by Eq. (39) corresponds to the region $x < 0$. Now at $t = 0$ we assume the packet to be far away from the barrier (see Fig. 4.4a) and as t increases the packet moves towards the barrier. At a much later time the reflected packet moves towards the

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*For $E > V_0$, $k > \beta$ (see Problem 4.6).

**This can be physically understood from the fact that since the wavefunction is finite in the region $x > 0$ (see Sec. 4.2) the packet can be thought of penetrating into the region $x > 0$ for a certain distance and then coming back (see the discussion at the end of this section and Problem 4.5); the corresponding optical problem is discussed in Chapter 11 of Ghatak and Thyagarajan (1978).

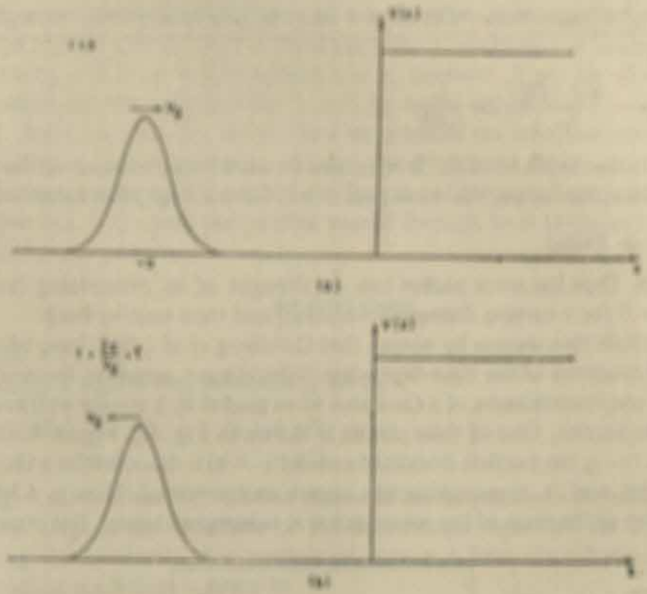

Fig. 4.4 (a) At $t = 0$ the wave packet is peaked around $x = -a$ and approaching the potential step with group velocity $v_g = \hbar k_0/m$. (b) At $t = (2a/v_g) + \tau$ the wave packet is again peaked around $x = -a$ but going away from the potential step. In general, the packet will also undergo dispersion which is not shown in the figure.

left (see Fig. 4.4b) with the same group velocity v_g. At intermediate times the incident and reflected waves interfere near $x = 0$ and the total wavefunction is quite complicated. In the region $x > 0$, the transmitted wave packet will be given by

$$\Psi_{tr} = \frac{1}{\sqrt{2\pi}}\int_0^\infty |A(k)| \frac{2k}{\sqrt{k^2+\kappa^2}} \exp[-\kappa(k)x - i\{\omega(k)t + \alpha(k) - \theta(k)\}]dk \quad (50)$$

where $\omega(k)$ is given by Eq. (41) and use has been made of the fact that the amplitude of the transmitted wave packet is given by (see Eq. 6)

$$C = \frac{2k}{k+i\kappa}A = \frac{2k}{(k^2+\kappa^2)^{1/2}}e^{-i\alpha(k)}A \quad (51)$$

Further, if we make Taylor expansions of $\omega(k)$, $\alpha(k)$ and $\theta(k)$ around $k = k_0$ and retain terms up to first order we would get

$$\Psi_{tr} \approx \frac{\exp[-i\{\omega(k_0)t + \alpha(k_0) - \theta(k_0)\}]}{\sqrt{2\pi}}\int_0^\infty |A(k)| \frac{2k}{(k^2+\kappa^2)^{1/2}}$$

$$\times \exp\left[-\kappa(k)x - iv_g(k-k_0)\left(t - \frac{a + \tau/2}{v_g}\right)\right] \quad (52)$$

where use has been made of Eqs. (47), (48) and (49). The above equation implies that ψ_{tr} has maximum value at $t = (a + \tau/2)/v_g$ and would be negligibly small for

$$\left| t - \frac{a + \tau/2}{v_g} \right| \gtrsim \frac{1}{v_g \Delta k} \tag{53}$$

where Δk is the width of $A(k)$. It may also be noted that because of the exponentially decaying factor, the wave packet will have a negligible value for

$$x \gtrsim 1/\kappa(k_0) \tag{54}$$

at all times. Thus the wave packet can be thought of as penetrating into the region $x > 0$ for a certain distance $[\sim 1/\kappa(k_0)]$ and then coming back.

We conclude this section by noting that Goldberg *et al.* (1967) have obtained numerical solutions of the time dependent Schrödinger equation to study the reflection and transmission of a Gaussian wave packet by a square well and by a rectangular barrier. One of their results is shown in Fig. 4.5. Figure 4.5(a) tells us that at $t = t_0$ the particle (localized around $x = a$) is described by a Gaussian wave packet and is approaching the square well potential. Figures 4.5(b), (c) and (d) give us the form of the wave packet at subsequent times. It is interesting

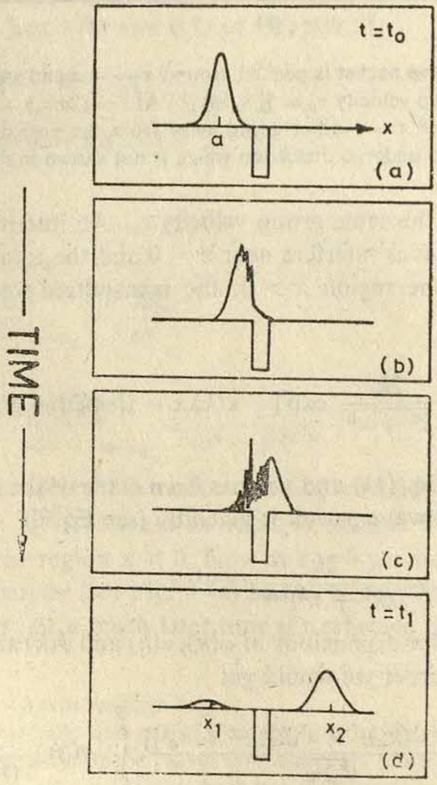

Fig. 4.5 Reflection and transmission of a wave packet by a square well; the mean energy of the packet corresponds to the well depth (adapted from Goldberg *et al.*, 1967).

to note that at $t = t_1$ the particle is described by two packets one centred around $x = x_1$ and the other around $x = x_2$. Thus at $t = t_1$ the particle is at both the places in the sense that there are finite probabilities of finding the particle around $x = x_1$ as well as around $x = x_2$; however, if we try to determine the position of the particle then it will be found either near $x = x_1$ or near $x = x_2$. A similar situation arises when we consider the reflection and transmission of a wave packet by a potential step (see Problem 4.6). We may mention that the arguments are the same as in the case of Young's double hole experiment (see Sec. 1.5) where the particle passed through both the holes to produce the interference pattern.

PROBLEMS

PROBLEM 4.1

Consider a square well potential given by

$$\begin{aligned} V(x) &= -V_0 \qquad |x| < a/2 \\ &= 0 \qquad\quad |x| > a/2 \end{aligned} \tag{55}$$

(see Fig. 4.6). In Sec. 3.6.2 we had discussed the bound states for such a potential well. Discuss the solutions of the Schrödinger equation for $E > 0$ and assuming the incidence of a particle of energy E from the left show that the transmission coefficient is given by

$$T = \left[1 + \frac{1}{4}\left(\frac{k}{k_2} - \frac{k_2}{k}\right)^2 \sin^2(k_2 a)\right]^{-1} \tag{56}$$

where

$$k = (2mE/\hbar^2)^{1/2}, \quad k_2 = [2m(E + V_0)/\hbar^2]^{1/2} \tag{57}$$

Notice that transmission resonance occurs when $k_2 a = n\pi$. Interpret the result physically. It may be mentioned that such transmission resonances occur in the

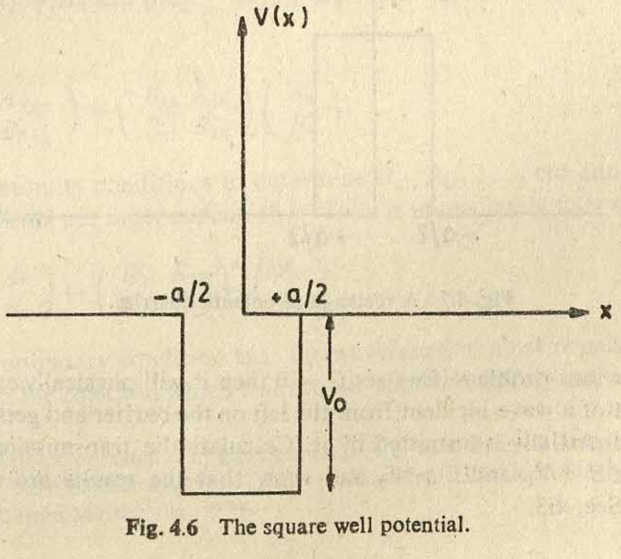

Fig. 4.6 The square well potential.

scattering of electrons from noble gases such as argon and neon. This is known as the Ramsauer–Townsend effect. (See also Sec. 19.5.2 and Mott and Massey, 1933, p. 133.)

PROBLEM 4.2

Consider a potential barrier of the form (see Fig. 4.7)

$$\begin{aligned} V(x) &= V_0 \qquad |x| < a/2 \\ &= 0 \qquad |x| > a/2 \end{aligned} \tag{58}$$

In the region $|x| > a/2$, the solution of the Schrödinger equation can be written as

$$\begin{aligned} \psi &= Ae^{ikx} + Be^{-ikx} \qquad x < -a/2 \\ &= Fe^{ikx} + Ge^{-ikx} \qquad x > +a/2 \end{aligned} \tag{59}$$

Using continuity conditions at $x = \pm a/2$ show

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix} \begin{pmatrix} F \\ G \end{pmatrix} \tag{60}$$

where

$$\left.\begin{aligned} R_{11} &= \left[\cosh \kappa a + \frac{i\sigma}{2} \sinh \kappa a \right] e^{ika} \\ R_{22} &= \left[\cosh \kappa a - \frac{i\sigma}{2} \sinh \kappa a \right] e^{-ika} \\ R_{12} &= (i\tau/2) \sinh \kappa a = -R_{21} \\ \sigma &= (\kappa/k) - (k/\kappa), \ \tau = (\kappa/k) + (k/\kappa) \end{aligned}\right\} \tag{61}$$

k and κ are defined through Eq. (19). For $E < V_0$, κ is real and for $E > V_0$, κ is pure imaginary.

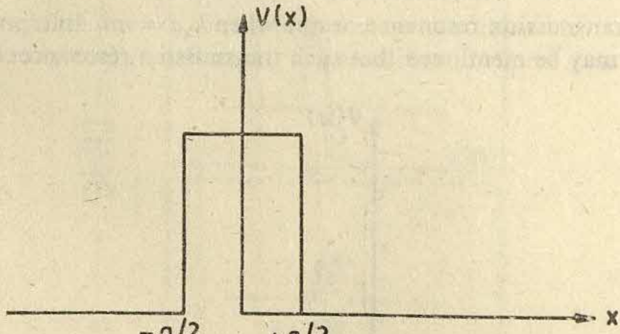

Fig. 4.7 A rectangular potential barrier.

PROBLEM 4.3

In the previous problem if we set $G = 0$ then it will physically correspond to the situation of a wave incident from the left on the barrier and getting partially reflected and partially transmitted by it. Calculate the transmission coefficient for the cases $E < V_0$ and $E > V_0$ and show that the results are the same as obtained in Sec. 4.3.

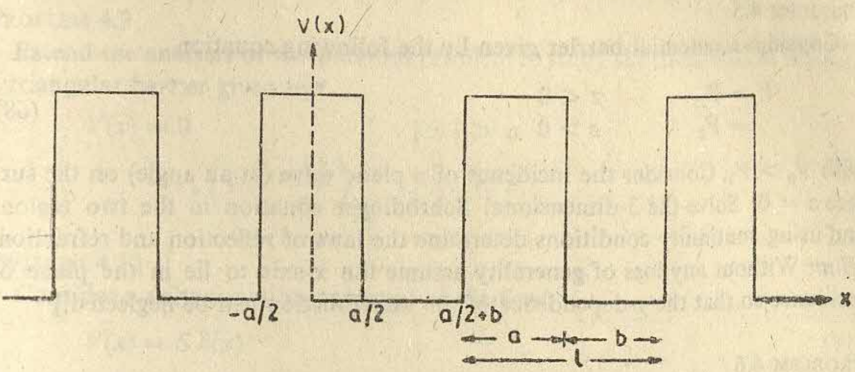

Fig. 4.8 A periodic potential.

PROBLEM 4.4

Consider a periodic potential of the form* (see Fig. 4.8)

$$\begin{aligned} V(x) &= V_0 \qquad & -a/2 < x < +a/2 \\ &= 0 \qquad & a/2 < x < a/2 + b \end{aligned} \tag{62}$$

with

$$V(x+l) = V(x) \tag{63}$$

where $l = a + b$ represents the periodicity of the potential. We label the nth valley (of the periodic potential) as

$$(n-1)l + a/2 < x < nl - a/2 \tag{64}$$

with $n = 0, \pm 1, \pm 2, \ldots$ and write the solution of the Schrödinger equation in the nth valley as

$$\psi(x) = A_n \exp [ik(x - nl)] + B_n \exp [-ik(x - nl)] \tag{65}$$

We write

$$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix} \begin{pmatrix} A_n \\ B_n \end{pmatrix} \tag{66}$$

Use the continuity conditions to determine $R_{11}, R_{12}, \ldots$ etc. and show that the matrix elements are independent of n. Thus it immediately follows that

$$\begin{pmatrix} A_n \\ B_n \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix}^n \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} \tag{67}$$

Using the boundary condition that the wavefunction must remain finite at $x \to \pm \infty$ obtain the equation which leads to the allowed and forbidden energy bands.

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*Such a periodic potential is of great importance in band theory of solids (see. e.g., Kittel, 1956, Dekker, 1957, McKelvey, 1966). The present method of solution for the periodic potential is adapted from Merzbacher (1970).

PROBLEM 4.5

Consider a potential barrier given by the following equation

$$\begin{aligned} V &= V_1 \qquad & z < 0 \\ &= V_2 \qquad & z > 0 \end{aligned} \tag{68}$$

with $V_2 > V_1$. Consider the incidence of a plane wave (at an angle) on the surface $z = 0$. Solve the 3-dimensional Schrödinger equation in the two regions and using continuity conditions determine the laws of reflection and refraction. [*Hint*: Without any loss of generality assume the x-axis to lie in the plane of incidence so that the y-dependence of the wavefunction can be neglected.]

PROBLEM 4.6

In Sec. 4.4 we had considered the reflection of a wave packet by a potential step and had assumed that the component waves, the superposition of which gives the wave packet, correspond to $E < V_0$. Discuss the reflection (and) transmission of a wave-packet whose component waves correspond to $E > V_0$.

PROBLEM 4.7

For the potential step problem (see Sec. 4.2) the wavefunction in the region $x > 0$ is of the form $e^{-\kappa x}$ Calculate $\langle x \rangle$, $\langle x^2 \rangle$ and show that $\Delta x \sim 1/\kappa$.

[*Hint*: $\langle x \rangle = \int_0^\infty x e^{-2\kappa x}\, dx \Big/ \int_0^\infty e^{-2\kappa x}\, dx$, etc.]

PROBLEM 4.8

Consider a potential energy variation given by (see Fig. 4.9)

$$\begin{aligned} V(x) &= 0 \qquad & x < -a \text{ and } x > 0 \\ &= V_0\left(1 + \frac{x}{a}\right) \qquad & -a < x < 0 \end{aligned} \tag{69}$$

Obtain an exact solution of the Schrödinger equation and obtain expressions for the transmission coefficient.

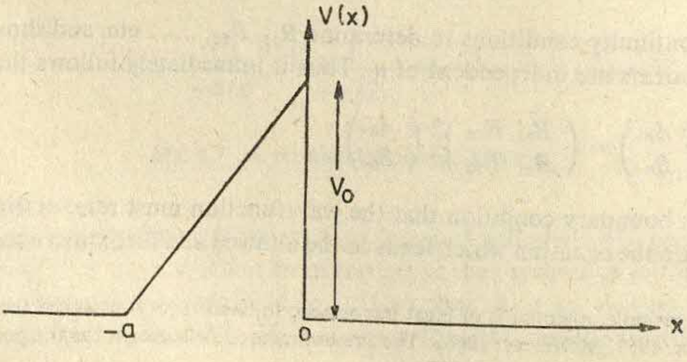

Fig. 4.9 The potential energy variation given by Eq. (69).

PROBLEM 4.9

Extend the analysis of the previous problem to study the transmission through a triangular barrier given by*

$$\begin{aligned} V(x) &= 0 & \qquad |x| > a \\ &= V_0\left(1 - \frac{|x|}{a}\right) & \qquad |x| < a \end{aligned} \tag{70}$$

PROBLEM 4.10

Consider a delta function potential of the form

$$V(x) = S\,\delta(x) \tag{71}$$

Show that the transmission amplitude ($= F/A$) and the transmission coefficient ($= |F/A|^2$) are

$$ik\Big/\left(ik - \frac{mS}{\hbar^2}\right)$$

and

$$E/(E + mS^2/2\hbar^2)$$

respectively.

SOLUTIONS

SOLUTION 4.1

For a particle incident from the left, the solutions of the Schrödinger equation are

$$\begin{aligned} \psi &= Ae^{ikx} + Be^{-ikx} & \qquad x < -a/2 \\ &= Ce^{ik_2x} + De^{-ik_2x} & \qquad a/2 < x < -a/2 \\ &= Fe^{ikx} & \qquad x > a/2 \end{aligned} \tag{72}$$

The continuity conditions at $x = \pm\, a/2$ immediately lead to the transmission coefficient ($= |F/A|^2$). For $k_2a = n\pi$ the transmission coefficient is unity and this is again similar to what happens in a Fabry-Perot etalon (see also Sec. 4.3).

SOLUTION 4.4

The continuity conditions immediately give

$$\begin{aligned} R_{11} &= e^{ikb}\left[\cosh \kappa a - \frac{i\sigma}{2}\sinh \kappa a\right] \\ R_{12} &= -\frac{i\tau}{2}\sinh \kappa a\, e^{ik(a+b)} \\ R_{22} &= R_{11}^*, \quad R_{21} = R_{12}^* \end{aligned} \tag{73}$$

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*Tunnelling through such a barrier is of importance in solid state physics (see, e.g., Roy and Ghatak, 1971).

where σ and τ are defined through Eq. (61). Now the eigenvalues of the R matrix are given by

$$\lambda_{\pm} = \frac{1}{2}\left[\eta \pm \sqrt{\eta^2 - 4}\right] \tag{74}$$

where we have used the fact that $R_{11}R_{22} - R_{12}R_{21} = 1$ and $\eta = R_{11} + R_{22} = R_{11} + R_{11}^*$ which is a real quantity. Further, any column vector can also be written as a sum of two eigenvectors and therefore we may write

$$\begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \begin{pmatrix} a_+ \\ b_+ \end{pmatrix} + \begin{pmatrix} a_- \\ b_- \end{pmatrix}$$

where $\begin{pmatrix} a_+ \\ b_+ \end{pmatrix}$ and $\begin{pmatrix} a_- \\ b_- \end{pmatrix}$ are eigenvectors corresponding to the eigenvalues λ_+ and λ_- respectively. Thus

$$\begin{pmatrix} A_n \\ B_n \end{pmatrix} = R^n \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} = \lambda_+^n \begin{pmatrix} a_+ \\ b_+ \end{pmatrix} + \lambda_-^n \begin{pmatrix} a_- \\ b_- \end{pmatrix} \tag{75}$$

Clearly if $|\eta| > 2$, the two roots are real and the wavefunction will diverge either for $x \to \infty$ or $x \to -\infty$. Thus we must have

$$|\eta| \leqslant 2 \tag{76}$$

for which $|\lambda_+| = |\lambda_-| = 1$. Since η is real we can always write

$$\frac{1}{2}\eta = \cos\varphi \tag{77}$$

or

$$\cos\varphi = \cosh\kappa a \cos kb + \frac{\sigma}{2}\sinh\kappa a \sin kb \tag{78}$$

For $kb = N\pi$, it immediately follows that Eqs. (76) and (78) cannot be satisfied and hence such energy values are not allowed. By plotting $\eta/2$ as a function of E one can readily obtain regions of allowed and forbidden energies—these are the energy bands and are discussed in any book on solid state physics.

For $E > V_0$, the corresponding equation becomes

$$\cos\varphi = \cos k_1 a \cos kb - \frac{k_1^2 + k^2}{2kk_1}\sin k_1 a \sin kb \tag{79}$$

which again leads to the allowed and forbidden energy bands.

In order to get a numerical appreciation, we consider the limiting case of $V_0 \to \infty$ and $a \to 0$ such that

$$\frac{mb}{\hbar^2} V_0 a \to P$$

(This is known as the Kronig-Penney model). For such a case Eq. (78) becomes

$$\cos\varphi = \frac{P}{kb}\sin kb + \cos kb \tag{80}$$

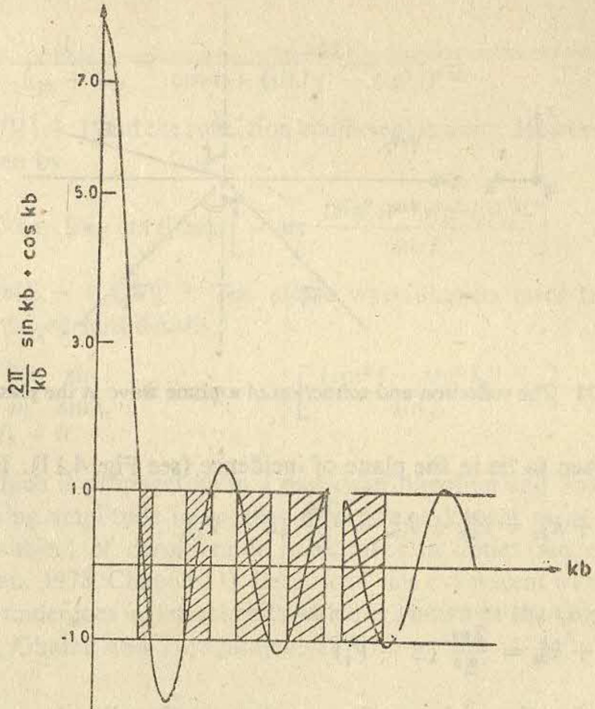

Fig. 4.10 The shaded regions correspond to $|\cos\varphi| < 1$ and therefore the corresponding energies are allowed.

In Fig. 4.10 we have plotted the right hand side as a function of *kb* for $P = 2\pi$. The shaded region corresponds to allowed energies. Notice the formation of allowed and forbidden energy bands.

SOLUTION 4.5

The three dimensional Schrödinger equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}[E - V(z)]\,\psi(x,y,z) = 0 \tag{81}$$

with

$$\begin{aligned} V(z) &= V_1 \qquad z < 0 \\ &= V_2 \qquad z > 0 \end{aligned} \tag{82}$$

can easily be solved by using the method of separation of variables. The solution corresponding to the reflection and transmission of a particle is given by

$$\begin{aligned} \psi &= A\exp[i(k_{1x}x + k_{1z}z)] + B\exp[i(k_{2x}x - k_{2z}z)], \quad z < 0 \\ &= C\exp[i(k_{3x}x + k_{3z}z)] \qquad\qquad\qquad\qquad\qquad\quad z > 0 \end{aligned} \tag{83}$$

where we have assumed (without any loss of generality) that $k_y = 0$, i.e., the

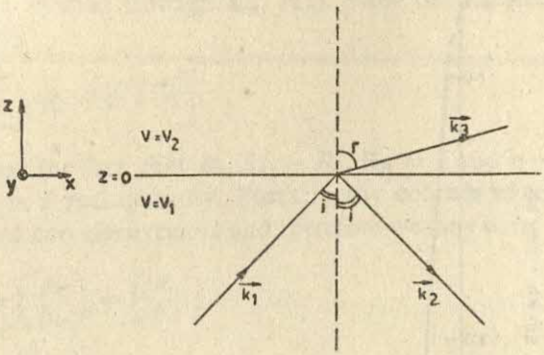

Fig. 4.11 The reflection and refraction of a plane wave at the plane $z = 0$.

x-axis is chosen to lie in the plane of incidence (see Fig. 4.11). Further,

$$k_{1x}^2 + k_{1z}^2 = k_{2x}^2 + k_{2z}^2 = \frac{2m}{\hbar^2}(E - V_1) \tag{84}$$

and

$$k_{3x}^2 + k_{3z}^2 = \frac{2m}{\hbar^2}(E - V_2) \tag{85}$$

For the wavefunction to be continuous at $z = 0$ (for all values of x) we must have

$$k_{1x} = k_{2x} = k_{3x} \tag{86}$$

Thus $k_{2z} = k_{1z}$ [see Eq. (84)] implying that the angles of incidence and reflection are equal. Further, if i and r represent the angles of incidence and refraction then

$$\sin i = \frac{k_{1x}}{(k_{1x}^2 + k_{1z}^2)^{1/2}} = \left(\frac{\hbar^2}{2m(E - V_1)}\right)^{1/2} k_{1x} \tag{87}$$

and a similar relation for $\sin r$, from which we immediately obtain

$$\frac{\sin i}{\sin r} = \left(\frac{E - V_2}{E - V_1}\right)^{1/2} \tag{88}$$

which is nothing but Snell's law. The critical angle is given by

$$\sin i_c = \left(\frac{E - V_2}{E - V_1}\right)^{1/2} \tag{89}$$

For $i > i_c$, k_{3z} is pure imaginary and there is an exponentially decaying wave in the region $z > 0$.

Now, continuity of ψ and $d\psi/dz$ at $z = 0$ gives [cf. Eqs. (5) and (6)]

$$\frac{B}{A} = \frac{k_{1z} - k_{3z}}{k_{1z} + k_{3z}} = \frac{\cos i - (\sin^2 i_c - \sin^2 i)^{1/2}}{\cos i + (\sin^2 i_c - \sin^2 i)^{1/2}} \tag{90}$$

and

$$\frac{C}{A} = \frac{2k_{1z}}{k_{1z} + k_{3z}} = \frac{2\cos i}{\cos i + (\sin^2 i_c - \sin^2 i)^{1/2}} \tag{91}$$

For $i > i_c$, $|B/A| = 1$ and the reflection coefficient is unity. However, the wavefunction is given by

$$\psi = C \exp[i\kappa x \sin i] \exp\left[-\kappa z \frac{(\sin^2 i - \sin^2 i_c)^{1/2}}{\sin i_c}\right] \tag{92}$$

where $\kappa = [2m(E - V_2)/\hbar^2]^{1/2}$. The above wavefunction gives the following expression for the current density

$$J_x = \frac{\hbar\kappa}{m}\,\frac{\sin i}{\sin i_c}\,|C|^2 \exp - 2\kappa\left[\frac{(\sin^2 i - \sin^2 i_c)^{1/2}}{\sin i_c}\, z\right] \tag{93}$$
$$J_y = J_z = 0$$

Such a wave which is propagating in a particular direction and has an exponentially decreasing amplitude in another direction is known as an evanescent wave and is a subject of considerable importance in optics (see, e.g., Ghatak and Thyagarajan, 1978, Chapter 11). Because of this evanescent wave, the beam (on reflection) undergoes a lateral shift which is known as the Goos-Hanchen effect (see, e.g., Ghatak and Thyagarajan, 1978).

SOLUTION 4.6

For $E > V_0$, the incident, reflected and transmitted wave packets would be [cf. Eqs. (43), (44) and (52)]

$$\Psi_{\text{inc}}(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\beta}^{\infty} |A(k)| \exp[i\{kx - \omega(k)t + \phi(k)\}]\, dk \tag{94}$$

$$\Psi_{\text{ref}}(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\beta}^{\infty} |A(k)| \frac{k - \sqrt{k^2 - \beta^2}}{k + \sqrt{k^2 - \beta^2}} \exp[-i\{kx + \omega(k)t - \phi(k)\}]\, dk \tag{95}$$

$$\Psi_{\text{tr}}(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\beta}^{\infty} |A(k)| \frac{2k}{k + \sqrt{k^2 - \beta^2}} \exp[i\{\sqrt{k^2 - \beta^2}\, x - \omega(k)t + \phi(k)\}]\, dk \tag{96}$$

where we have used Eqs. (5) and (6) and the fact that

$$k_1 = \left[\frac{2m(E - V_0)}{\hbar^2}\right]^{1/2} = [k^2 - \beta^2]^{1/2} \tag{97}$$

Notice that since B/A and C/A are real [see Eqs. (5) and (6)], there are no additional phase factors appearing in the exponent. Thus the centre of the wave packet associated with the incident, reflected and transmitted waves would be

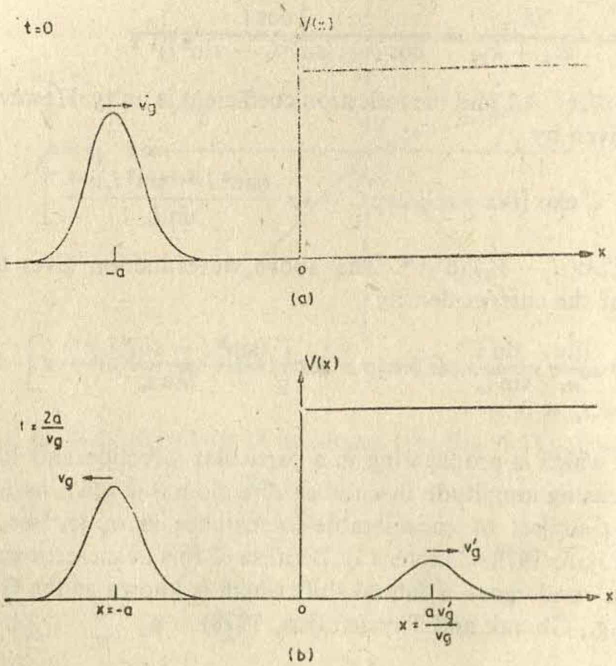

Fig. 4.12 The reflection and refraction of a wave packet at a potential step. The discussion at the end of Sec. 4.4 is also valid here.

[cf. Eqs. (45) and (46)]

$$\begin{aligned} x_c^{\text{inc}} &= -a + v_g t \\ x_c^{\text{ref}} &= a - v_g t \\ x_c^{\text{tr}} &= -\frac{a v_g'}{v_g} + v_g' t \end{aligned} \tag{98}$$

where*

$$v_g' = \frac{\hbar\sqrt{k_0^2-\beta^2}}{m} \tag{99}$$

which represents the group velocity in the region $x > 0$ (see Fig. 4.12).

---

*The expression for v_g' follows from the fact that

$$\begin{aligned}(k^2-\beta^2)^{1/2}x-\omega t &= \left[(k_0^2-\beta^2)^{1/2}+\frac{k_0}{(k_0^2-\beta^2)^{1/2}}(k-k_0)+\dots\right]x \\ &\quad - \left[\omega(k_0)+(k-k_0)\left.\frac{d\omega}{dk}\right|_{k=k_0}+\dots\right]t \\ &= \left[(k_0^2-\beta^2)^{1/2}x-\omega(k_0)t\right]+(k-k_0)\frac{k_0}{\sqrt{k_0^2-\beta^2}} \\ &\quad \times\left\{x-\frac{\sqrt{k_0^2-\beta^2}\left.\frac{d\omega}{dk}\right|_{k=k_0}}{k_0}\right\}t+\dots\end{aligned}$$

SOLUTION 4.8

The Schrödinger equation can be rewritten in the form

$$\frac{d^2\psi}{d\xi^2} + \gamma^2\psi(\xi) = 0 \qquad \xi < -\xi_1 \quad \text{and}\ \xi > \xi_2 \tag{100}$$

$$\frac{d^2\psi}{d\xi^2} - \xi\psi(\xi) = 0 \qquad -\xi_1 < \xi < \xi_2 \tag{101}$$

where

$$\begin{aligned} &\xi = \varepsilon(1 + x/a) - \xi_1 \\ &\gamma^2 = \xi_1 = \varepsilon\,\frac{E}{V_0},\ \xi_2 = \varepsilon - \xi_1 \\ &\varepsilon = [2m\,V_0\,a^2/\hbar^2]^{1/3} \end{aligned} \tag{102}$$

The solutions are

$$\begin{aligned} \psi(\xi) &= e^{i\gamma\xi} + r\,e^{-i\gamma\xi} && \xi < -\xi_1 \\ &= AU_1(-\xi) + BU_2(-\xi) && -\xi_1 < \xi < \xi_2 \\ &= t\,e^{i\gamma\xi} && \xi > \xi_2 \end{aligned} \tag{103}$$

The U_1 and U_2 functions (along with their derivatives) have been tabulated by Smirnov (1960) and are related to the Bessel functions through the following relations,

$$\begin{aligned} U_1(s) &= 3^{-1/3}\,\Gamma(2/3)\,\sqrt{s}\,J_{-1/3}\,(2/3\ s^{3/2}) \\ U_2(s) &= 3^{1/3}\,\Gamma(4/3)\,\sqrt{s}\,J_{1/3}\,(2/3\ s^{3/2}). \end{aligned} \tag{104}$$

Applying the boundary condition at $\xi = -\xi_1$ and $\xi = \xi_2$ we can easily get an expression for the tunneling coefficient $T = |t|^2$.

SOLUTION 4.10

In the results given in Sec. 4.3 take the limit of $V_0 \to \infty$ and $a \to 0$ such that the product $V_0\,a \to s$.

CHAPTER FIVE

Simple Solutions of the Schrödinger Equation II: Three-Dimensional Considerations

5.1 Introduction

In Chapter 3 we had discussed the stationary states of the one-dimensional Schrödinger equation; the corresponding considerations for the three-dimensional equation are very straightforward. For example, by using the method of separation of variables, the solution of the time dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{r})\,\Psi \tag{1}$$

is of the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp\left[-iEt/\hbar\right] \tag{2}$$

where $\psi(\mathbf{r})$ is the solution of the eigenvalue equation [cf. Eq. (6) of Chapter 3]

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{3}$$

and

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V(\mathbf{r}) \tag{4}$$

represents the Hamiltonian operator and E the energy eigenvalue. The potential energy function has been assumed to be independent of time. In general, the eigenvalues can have a discrete set along with a continuous range of eigenvalues and the general solution of Eq. (1) is of the form [cf. Eq. (11) of Chapter 3]

$$\Psi(\mathbf{r}, t) = \sum_n a_n\, \psi_n(\mathbf{r}) \exp\left(-iE_nt/\hbar\right)$$

where $\sum_n$ denotes a sum over the discrete modes and an integration over the continuum.

Equation (3) is usually written in the form

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[E - V(\mathbf{r})\right]\psi(\mathbf{r}) = 0 \tag{5}$$

which is known as the 3-dimensional time-independent Schrödinger equation.

As in Chapter 3, the wavefunction satisfies continuity and boundary conditions. Thus

(1) The wavefunction and its gradient are continuous everywhere as long as the potential energy function is finite.

(2) The wavefunction should also be single valued everywhere so that it corresponds to a definite physical situation.

(3) For a degenerate state any linear combination of the degenerate eigenfunctions is also a possible eigenfunction.

The orthogonality of the wavefunctions can be proved by using a method similar to the one used in Sec. 3.4. Indeed, instead of Eqs. (14) and (15) of Chapter 3, we will have

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n + V(\mathbf{r})\psi_n = E_n\psi_n \tag{6}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_k + V(\mathbf{r})\psi_k = E_k\psi_k \tag{7}$$

If we multiply Eq. (6) by ψ_k^* and multiply the complex conjugate of Eq. (7) by ψ_n and subtract, we would get

$$-\frac{\hbar^2}{2m}\int \nabla\cdot[\psi_k^*\nabla\psi_n - \psi_n\nabla\psi_k^*]\,d\tau = (E_n - E_k^*)\int\psi_k^*\psi_n\,d\tau$$

By using Gauss theorem, the LHS becomes a surface integral

$$-\frac{\hbar^2}{2m}\int[\psi_k^*\nabla\psi_n - \psi_n\nabla\psi_k^*]\cdot d\mathbf{s}$$

which would vanish if the volume integral is over the entire space. Thus, as in Sec. 3.4 we will have

$$E_n = E_n^* \tag{8}$$

proving that all eigenvalues are real and the wavefunctions belonging to different energy levels are orthogonal. By appropriate normalization we can always have

$$\int\psi_k^*\psi_n\,d\tau = \delta_{kn} \tag{9}$$

which is the orthonormality condition. For degenerate states one can always construct appropriate linear combinations so that the orthonormality condition is satisfied (see Problem 3.3).

In Sec. 5.2 we will show that as long as the potential is spherically symmetric (i.e., as long as the potential depends only on the magnitude of the distance from a fixed point) the angular part of the wavefunction is a spherical harmonic and the potential energy function enters only in the radial part of the equation. In Sec. 5.3 we will solve the hydrogen atom problem and obtain the discrete states for the Coulomb potential and will show that the results are consistent with the experimental data.

In the Problems we will discuss several other examples for which the exact solution of the Schrödinger equation are known. However, once again, for most problems of practical interest it is not possible to obtain exact solutions and one has to resort to approximate and numerical methods, some of which are discussed in Chapters 11, 12, 13 and 16.

5.2 Motion in a Spherically Symmetric Field

One of the most important problems in quantum mechanics is the motion of a particle in a potential which depends only on the magnitude of the distance from a fixed point

$$V(\mathbf{r}) = V(r) \tag{10}$$

Now, in spherical polar co-ordinates, we have

$$\begin{aligned}\nabla^2\psi &= \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi \\ &= \frac{1}{r}\frac{\partial^2}{\partial r^2}\left(r\psi\right) + \frac{1}{r^2}\Lambda\psi \end{aligned} \tag{11}$$

where the operator Λ is defined through the following equation

$$\Lambda\psi \equiv \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} \tag{12}$$

From the above equations we note the following very important feature. As long as the potential is spherically symmetric, the angular part of the Hamiltonian is fixed. We therefore expect the angular dependence of the wavefunctions for such problems to be the same in all cases.

We can determine the angular part by writing

$$\psi(r, \theta, \varphi) = R(r)\ Y(\theta, \varphi) \tag{13}$$

Substituting this into Eq. (5), we have

$$\left[\frac{1}{r}\frac{d^2}{dr^2}\left(rR\right) + \frac{2m}{\hbar^2}\left\{E - V(r)\right\}R\right]Y(\theta, \varphi) + \frac{R}{r^2}\ \Lambda Y(\theta, \varphi) = 0$$

Dividing by RY/r^2, we obtain

$$r^2\left\{\frac{1}{rR(r)}\frac{d^2}{dr^2}(rR) + \frac{2m}{\hbar^2}\left(E - V(r)\right)\right\} = -\frac{\Lambda Y(\theta, \varphi)}{Y(\theta, \varphi)} = \lambda \tag{14}$$

where we have set the terms equal to a constant λ because the left hand side of Eq. (14) depends only on r while the other term depends only on θ and φ. The above equation gives us the eigenvalue equation

$$\Lambda Y(\theta, \varphi) = -\lambda Y(\theta, \varphi) \tag{15}$$

Now, in Chapter 6 we will show that the operator Λ is related to the quantum mechanical angular momentum operator $\mathbf{L}$; indeed

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] = -\hbar^2\Lambda \tag{16}$$

(see Sec. 6.2), here $L^2 = L_x^2 + L_y^2 + L_z^2$; L_x, L_y and L_z representing the Cartesian components of $\mathbf{L}$. We will also show that the eigenvalues of the operator L^2 are

$$l(l+1)\hbar^2; \qquad l = 0, 1, 2, \ldots.$$

i.e., well behaved solutions are obtained when

$$\lambda = l(l+1) \tag{17}$$

the corresponding eigenfunctions being the spherical harmonics

$$Y_{lm}(\theta, \varphi), \qquad m = -l, -l+1, \ldots l \tag{18}$$

(see Secs. 6.3 and 6.4 and Appendix I). Thus Eq. (14) takes the form

$$\frac{d^2R}{dr^2} + \frac{1}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right]R(r) = 0 \tag{19}$$

which is known as the radial part of the Schrödinger equation. If we define a new radial function

$$u(r) = rR(r) \tag{20}$$

and use Eq. (17), then Eq. (14) becomes

$$\frac{d^2u(r)}{dr^2} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\,\hbar^2}{2mr^2}\right]u(r) = 0 \tag{21}$$

Comparing this with Eq. (12) of Chapter 3, we may consider the radial motion to be similar to the one-dimensional motion of a particle in a potential

$$V(r) + \frac{l(l+1)\,\hbar^2}{2mr^2} \tag{22}$$

Now, according to classical mechanics, if a particle (of mass m) is rotating (with speed v) in a circular orbit of radius r then the angular momentum associated with such a circular motion is $L = mvr$. To maintain such a circular motion there must be a centripetal force given by

$$\mathbf{F} = -\frac{mv^2}{r}\hat{\mathbf{r}} = -\frac{L^2}{mr^3}\hat{\mathbf{r}} \tag{23}$$

where the negative sign implies that the force should be directed towards the origin. The corresponding potential energy is $-L^2/2mr^2$ which should be supplied by $V(r)$ and hence the effective potential is $V(r) + L^2/2mr^2$ which is consistent with Eq. (21) if we replace L^2 by $l(l+1)\hbar^2$.

5.3 The Hydrogen Atom

Since the potential experienced by the electron in a hydrogen atom possesses spherical symmetry, the angular part of the wavefunction is already determined. However, strictly the proton in the hydrogen atom cannot be regarded as fixed; but (as we will show now) the two body problem can always be reduced to a one body problem provided the potential energy depends only on the magnitude of the distance between the two particles (this is obviously true for the Coulomb potential). Now for the hydrogen atom problem, the Hamiltonian is

$$\begin{aligned} H &= \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|\mathbf{r}_1 - \mathbf{r}_2|) \\ &= -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(|\mathbf{r}_1 - \mathbf{r}_2|) \end{aligned} \tag{24}$$

where we have made use of the recipe of replacing $\mathbf{p}$ by $-i\hbar\nabla$; the subscripts 1 and 2 refer to electron and proton respectively. Further,

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \text{ etc.}$$

where (x_1, y_1, z_1) and (x_2, y_2, z_2) represent the co-ordinates of electron and proton respectively. The Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(|\mathbf{r}_1 - \mathbf{r}_2|)\right]\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\,\Psi(\mathbf{r}_1, \mathbf{r}_2) \quad (25)$$

It can easily be shown that if we try to separate the variables by assuming

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi_1(\mathbf{r}_1)\,\Psi_2(\mathbf{r}_2)$$

the variables will not separate. However, if we introduce the centre of gravity co-ordinates

$$= \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \quad (26)$$

and the relative co-ordinate

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \quad (27)$$

of the two particles, then the Schrödinger equation becomes*

$$\left[-\frac{\hbar^2}{2(m_1 + m_2)}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(r)\right]\Psi(\mathbf{R}, \mathbf{r}) = E\,\Psi(\mathbf{R}, \mathbf{r}) \quad (28)$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (29)$$

is known as the reduced mass. Since the potential does not depend on R at all, we write

$$\Psi(\mathbf{R}, \mathbf{r}) = \psi(\mathbf{r})\,\phi(\mathbf{R}) \quad (30)$$

and the Schrödinger equation is now separable giving the following equation for ϕ

$$-\frac{\hbar^2}{2M}\left[\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right]\phi = E_R\phi \quad (31)$$

the solution of which is

$$\phi \sim \exp[i\,\mathbf{P}\cdot\mathbf{R}/\hbar]; \quad E_R = \frac{\hbar^2 P^2}{2M} \quad (32)$$

---

*In obtaining Eq. (28) one has to use relations like

$$\frac{\partial\Psi}{\partial x_1} = \frac{\partial\Psi}{\partial x}\frac{\partial x}{\partial x_1} + \frac{\partial\Psi}{\partial y}\frac{\partial y}{\partial x_1} + \frac{\partial\Psi}{\partial z}\frac{\partial z}{\partial x_1} + \frac{\partial\Psi}{\partial X}\frac{\partial X}{\partial x_1} + \frac{\partial\Psi}{\partial Y}\frac{\partial Y}{\partial x_1} + \frac{\partial\Psi}{\partial Z}\frac{\partial Z}{\partial x_1}$$

$$= \frac{\partial\Psi}{\partial x} + \frac{m_1}{m_1 + m_2}\frac{\partial\Psi}{\partial x}, \quad \text{etc.}$$

where

$$M = m_1 + m_2$$

Equation (32) represents a plane wave and describes the motion of the hydrogen atom as a whole. On the other hand, $\psi(\mathbf{r})$ describes the internal motion of the atom and satisfies the equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V(r)\,\psi(\mathbf{r}) = E_r\,\psi(\mathbf{r}) \tag{33}$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ and E_r is the relative energy, i.e., it is the difference between the total energy E and the centre of mass energy E_R

$$E_r = E - E_R \tag{34}$$

Equation (33) is, of course, the same as that for a single particle in a potential V with the difference that the mass is replaced by the reduced mass and the co-ordinates are the relative co-ordinates.

In order to solve Eq. (33), we use the same method as discussed in Sec. 5.2 and write

$$\psi(\mathbf{r}) = R(r)\,Y_{lm}(\theta, \varphi) = \frac{u(r)}{r}\,Y_{lm}(\theta, \varphi) \tag{35}$$

The radial part of the wavefunction satisfies the following equation [see Eq. (19)]

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{r} - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R(r) = 0 \tag{36}$$

where we have removed the subscript on E since we are interested only in the energy levels associated with the relative motion and therefore we can take the centre of mass to be at rest. Further, we have set

$$\begin{aligned} V(r) &= -\frac{Zq^2}{4\pi\epsilon_0 r} && \text{(in } MKS \text{ units)} \\ &= -Ze^2/r && \text{(in } CGS \text{ units)} \end{aligned} \tag{37}$$

which represents the Coulomb potential (see Fig. 5.1) and the nuclear charge is assumed to be Zq so that the analysis will hold for hydrogen-like systems (like He^+, Li^{++}, . . .) as well*.

In order to solve Eq. (36) we introduce the dimensionless variable

$$\rho = \alpha r \tag{38}$$

---

*q and e represent the electronic charge in MKS and CGS units and ϵ_0 the permittivity of free space. In MKS units since the energy is measured in Joules [= 10^7 ergs] and distance is measured in metres [= 10^2 cm] we have

$$e = \left[\frac{q^2 \times 10^9}{4\pi\epsilon_n}\right]^{1/2} = \left[\frac{(1.6 \times 10^{-19})^2\,c \times 10^9}{4\pi \times 8.8542 \times 10^{-12}}\right]^{\frac{1}{2}} \simeq 4.8 \times 10^{-10} \text{ esu}$$

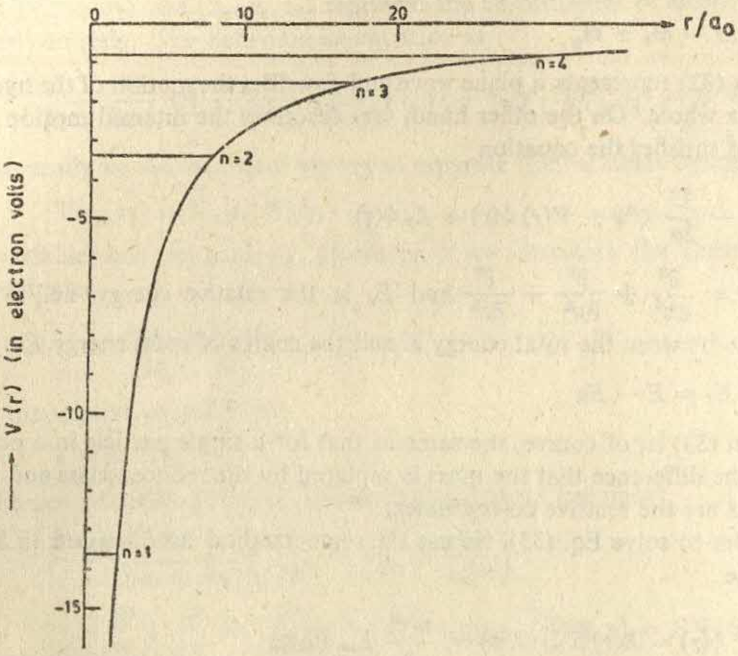

Fig. 5.1. The Coulomb potential for $Z = 1$. Negative E corresponds to discrete states and $E > 0$ represents the continuum.

where the parameter α is to be conveniently chosen later. Equation (36) becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left[\rho^2\frac{dR}{d\rho}\right]+\left[\frac{2\mu E}{\hbar^2\alpha^2}+\frac{2\mu}{\hbar^2}\frac{Ze^2}{\alpha\rho}-\frac{l(l+1)}{\rho^2}\right]R(\rho)=0 \qquad (39)$$

We choose*

$$\alpha^2=\frac{8\mu\,|E|}{\hbar^2}=-\frac{8\mu E}{\hbar^2} \qquad (40)$$

and set

$$\lambda=\frac{2\mu Ze^2}{\hbar^2\alpha}=\frac{Ze^2}{\hbar}\left(\frac{\mu}{2\,|E|}\right)^{1/2} \qquad (41)$$

Thus Eq. (39) becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left[\rho^2\frac{dR}{d\rho}\right]+\left[\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right]R(\rho)=0 \qquad (42)$$

In order to obtain an exact solution of Eq. (42) we introduce the function $F(\xi)$ defined through the relation**

$$R(\rho)=F(\rho)e^{-\rho/2} \qquad (43)$$

---

*We are looking for energy levels corresponding to bound states; therefore $E < 0$. The parameter α is not to be confused with the fine structure constant.

**As in the harmonic oscillator problem (see footnote on p. 89) if we look for solutions valid for $\rho \to +\infty$, we find that $R(\rho) \sim \rho^n \exp(\pm \rho/2)$ satisfies Eq. (42) for large values of ρ. This suggests that we look for a solution of the form given by Eq. (43).

On substitution we obtain

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left[\frac{\lambda - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right]F(\rho) = 0 \tag{44}$$

We now try a series solution of the form

$$F(\rho) = \sum_{p = 0, 1, \ldots} a_p\, \rho^{s+p} \tag{45}$$

Substituting this into Eq. (44) and equating the coefficients of the lowest powers of ρ, we obtain

$$s(s+1) - l(l+1) = 0$$

Thus

$$s = l \quad \text{or} \quad -l-1.$$

For $s = -l-1$, $F(\rho)$ would diverge for $\rho \to 0$; thus we should reject the solution $s = -l-1$ (see however the discussion at the end of this section). We also obtain the following recurrence relation

$$\frac{a_{p+1}}{a_p} = \frac{p + l + 1 - \lambda}{(p+1)(p+2l+2)} \tag{46}$$

For large values of p, $a_{p+1} \sim a_p/p$. This is also the ratio of terms in the expansion of exp (ρ). Thus if the series (45) does not terminate then $R(\rho)$ will behave as exp $(\frac{1}{2}\rho)$ for $\rho \to \infty$ and will diverge. We can make the series terminate by requiring that

$$\lambda = n = n' + l + 1 \tag{47}$$

then $a_{n'+1} = 0$. Since n' and l can be positive integers or zero, n can have the values 1, 2, 3, ... The number n is called the total quantum number. Using Eqs. (41) and (47) we obtain

$$E_n = -|E_n| = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}, \quad n = 1, 2, 3, \ldots. \tag{48}$$

Equation (48) gives the energy levels of the hydrogen atom. Before the development of quantum mechanics, it was known from experimental studies of the hydrogen atom spectrum, that the energy levels are given by

$$E_n = -E_R \cdot \frac{1}{n^2}, \quad n = 1, 2, \ldots. \tag{49}$$

and from observations E_R was found to be 13.6 eV. Bohr then devised a model* which gave Eq. (49) and predicted that E_R should be $me^4/2\hbar^2$. It was the first (and the most dramatic) success of Schrödinger's wave mechanics that it could reproduce this result from a basic equation of motion for the system.

The corresponding eigenfunctions are related to the associated Laguerre polynomials (see Appendix J). The complete solution is

$$\psi_{nlm} = R_{nl}(r)\, Y_{lm}(\theta, \varphi) \tag{50}$$

---

*This is now known as the old quantum theory.

and the first few R_{nl} are given by (see also Appendix J)

$$R_{10}(r) = (Z/a_0)^{3/2}\, 2 \exp(-Zr/a_0)$$
$$R_{20}(r) = (Z/2a_0)^{3/2}\left(2 - \frac{Zr}{a_0}\right) \exp(-Zr/2a_0) \tag{51}$$
$$R_{21}(r) = (Z/2a_0)^{3/2}\, \frac{Zr}{a_0\sqrt{3}} \exp(-Zr/2a_0)$$

where

$$a_0 = \frac{\hbar^2}{\mu e^2} \simeq 0.51\text{Å} \tag{52}$$

is known as the Bohr radius. The normalization constants are such that

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1 \tag{53}$$

Looking at Eq. (48) we see that the energy depends on the total quantum number n. Since for each n we have values of l ranging from 0 to $n - 1$ [see Eq. (47)] and for each value of l, the m values range from $-l$ to $+l$ [see Eq. (18)] there are

$$\sum_{l=0}^{n-1} (2l + 1) = n^2$$

states ψ_{nlm} belonging to a particular energy*. The degeneracy with respect to m is due to spherical symmetry of the potential energy function. But the l-degeneracy** is peculiar to the Coulomb field and is, in general, removed for non-Coulomb potentials (see e.g., Problem 5.6).

Returning to Eq. (45) it will be noticed that if one chooses the indicial equation

$$s = -l - 1$$

then for $l = 0$, $F(r) \sim 1/r$ or $\psi(r) \sim 1/r$ for small values of r. It is often wrongly stated that if ψ becomes infinite (as indeed the above choice does) then $|\psi|^2 d\tau$, which represents the probability of finding the particle in the volume element

---

*The states $l = 0, 1, 2, 3, 4, \ldots$ etc. are labelled as s, p, d, f, g, etc. so that a state $5g$ corresponds to $n = 5, l = 4$. In this connection we would like to clear a common misconception about the correspondence between Bohr-Sommerfeld orbits and these states. It is incorrect to picture—if one must picture—the s states as the one corresponding to a circular orbit. It is the very opposite since $l = 0$ should suggest that the electron moves in a straight line through the nucleus, the orbital angular momentum being zero. Thus the $5f$ state should be more nearly circular than the $5s$. There is, of course, no classical model which will be wholly satisfactory, see White (1934).

**This is so-called accidental degeneracy has been related to a symmetry of the Coulomb field in momentum space, see Fock (1935).

$d\tau$ will go to infinity*. This argument is not correct because the requirement

$$\underset{dr \to 0}{\mathrm{Lt}} \, |\psi|^2 r^2 dr = 0 \tag{54}$$

is satisfied by the choice $\psi \sim 1/r$. In order to understand the reason for rejecting the solution $\psi \sim 1/r$ we consider the solution of the Schrödinger equation [Eq. (33)] corresponding to $V(r) = 0$. If we assume $E = 0$, Eq. (33) becomes

$$\nabla^2 \psi = 0 \tag{55}$$

The radial part of this would be [cf. Eq. (36)]

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) - l(l+1)\, R(r) = 0 \tag{56}$$

For $l = 0$ one of the solutions of the above equation is $1/r$ which is however not a solution of Eq. (55); this follows from the fact that

$$\nabla^2(1/r) = 0 \tag{57}$$

for all values of r excepting at the point $r = 0$. Indeed**

$$\nabla^2(1/r) = -4\pi\delta(\mathbf{r}) = -4\pi\delta(x)\,\delta(y)\,\delta(z) \tag{58}$$

where $\delta(\mathbf{r})$ is the 3-dimensional Dirac delta function. We therefore see that the function $1/r$ is a solution of Eq. (56) but is not a solution of Eq. (55). This implies that as $r \to 0$ the wavefunction should not tend to ∞ as fast as $1/r$ otherwise ∇^2 operating on the wavefunction will give a delta function. Thus we have the boundary condition

$$\underset{r \to 0}{\mathrm{Lt}} \; r\psi(r) = 0 \quad \text{or} \quad u(0) = 0 \tag{59}$$

which immediately leads to the rejection of the solution corresponding to $s = -1$.

---

*Indeed the wavefunction $\psi(r) \sim 1/r \exp(-\alpha r)$ can be normalized because

$$\int |\psi|^2 d\tau = \int_0^\infty \frac{1}{r^2} \exp(-2\alpha r)\, 4\pi r^2\, dr = \frac{1}{2\alpha}.$$

**This can be easily seen if we consider the integral

$$\iiint_V \nabla^2(1/r)\, d\tau = \iiint_V \nabla \cdot (\nabla\, 1/r)\, d\tau = \iint_S (\nabla\, 1/r) \cdot \hat{\mathbf{r}}\, ds$$

$$= -\frac{1}{R^2} \iint R^2 d\Omega = -4\pi$$

where the volume V corresponds to a sphere (of radius R) whose centre is at the origin. The volume integral has been transformed to a surface integral by using Gauss theorem and on the surface of the sphere the integrand has a constant value equal to $-1/R^2$. Using the fact that $\nabla^2(1/r) = 0$ for $r \neq 0$ we immediately get Eq. (58); see the definition of the Dirac delta function in Appendix F.

5.3.1 THE PROBABILITY DISTRIBUTION FUNCTION FOR THE GROUND STATE OF THE HYDROGEN ATOM

For the ground state the wavefunction is spherically symmetric

$$\psi_{100} = \frac{1}{\sqrt{4\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-Zr/a_0\right) \tag{60}$$

If $P(r)\,dr$ represents the probability of finding the electron between r and $r + dr$, then

$$P(r)\,dr = |\psi_{100}|^2\, 4\pi r^2 dr = 4(Z/a_0)^3\, r^2 \exp\left[-2Zr/a_0\right] dr \tag{61}$$

Thus $P(r) = 0$ at $r = 0$ and at $r = \infty$ and has a maximum value at $r = a_0/Z$. This implies that the position of the electron is not certain but we can say for the hydrogen atom (for which $Z = 1$) that most probably the electron will be found around the Bohr radius. This is consistent with the uncertainty principle (see Problem 1.2). It may be noted that

$$\int_0^\infty P(r)\,dr = 1 \tag{62}$$

as it indeed should be. For higher excited states the probability density is maximum at a greater distance from the nucleus (see Fig. 5.2).

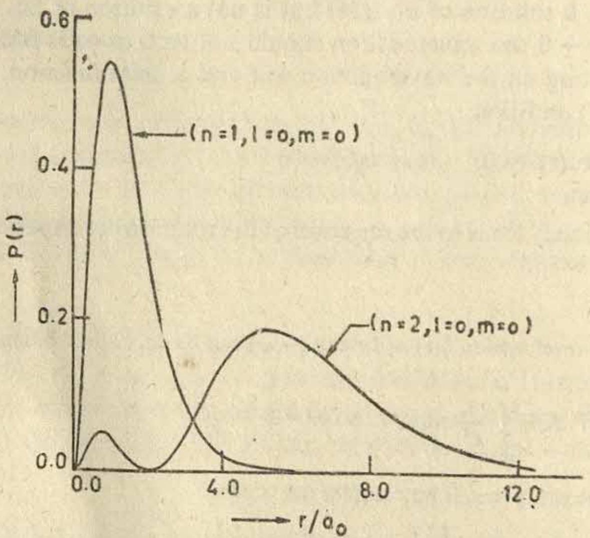

Fig. 5.2. The probability distribution function for $n = 1, l = 0, m = 0$ and $n = 2, l = 0, m = 0$ corresponding to $z = 1$.

PROBLEMS

PROBLEM 5.1

Consider a potential energy function of the form

$$\begin{aligned} V(r) &= 0, \qquad && 0 < r < a \\ &= \infty, && r > a \end{aligned} \tag{63}$$

which represents an infinitely deep spherically symmetric potential well of radius a. Obtain the energy levels and corresponding eigenfunctions.

PROBLEM 5.2

Consider a potential energy variation of the form

$$\begin{aligned} V(x, y, z) &= 0 \quad \text{for} \quad 0 < x < L, \ 0 < y < L, \ 0 < z < L \\ &= \infty, \quad \text{everywhere else} \end{aligned} \tag{64}$$

which represents a particle in an infinitely deep potential well inside a cube of side L. Determine the energy levels and the corresponding eigenfunctions.

PROBLEM 5.3

Problem 5.2 has an important application in the free electron theory of metals where the electron can be approximately assumed to be free and confined inside the box.

(a) Using the expression for the energy levels, show that the density of states is given by

$$g(E) = \frac{2(2m)^{3/2}V}{4\pi^2\hbar^3}\, E^{1/2} \tag{65}$$

where there is an extra factor of 2 which is due to the fact that each state can be occupied by 2 electrons.

(b) Assuming that the probability of finding an electron with energy E is given by the Fermi-Dirac function

$$F(E) = \frac{1}{1 + \exp\left[(E - E_F)/kT\right]} \tag{66}$$

show that

$$E_F(T = 0) = E_{F0} = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3};\ n = \frac{N}{V} \tag{67}$$

$$E_F(T) \simeq E_{F_0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F_0}}\right)^2 + \frac{\pi^4}{720}\left(\frac{kT}{E_{F_0}}\right)^4 \cdots\right] \tag{68}$$

where n represents the number of electrons per unit volume and in the last expression we have assumed $E_F/kT \gg 1$. Further, show that the electronic contribution to the specific heat is $\approx \frac{3R}{2}\left[\frac{\pi^2 kT}{3E_{F_0}}\right]$. Discuss the result physically. [*Hint*: Use the integrals

$$N = \int_0^\infty g(E)\, F(E)\, dE$$

$$\langle E \rangle = \int_0^\infty E g(E) F(E)\, dE$$

Integrate by parts and use the fact that dF/dE is very sharply peaked at $E = E_F$].

(c) In order to have a numerical appreciation of the previous problem, calculate E_{F_0} and the electronic contribution to specific heat for the sodium metal (assume 1 free electron per atom and density of sodium $\simeq 0.97$ g cm^{-3}).

PROBLEM 5.4

The deuteron nucleus consists of a neutron and proton. The neutron-proton interaction can be approximately described by the following spherically symmetric potential function*

$$\begin{aligned} V(r) &= \infty & r &< a \\ &= -V_0 & a &< r < a+b \\ &= 0 & r &> a+b \end{aligned} \tag{69}$$

(a) Obtain the transcendental equation determining the energy eigenvalues corresponding to the $l = 0$ state and show that if we assume $V_0 = 40$ MeV and the binding energy of deuteron to be 2.225 MeV then the value of $b \simeq 1.9 \times 10^{-13}$ cm.

(b) Also assuming $a \approx 0.4 \times 10^{-13}$ cm show that for the ground state

$$\langle r^2 \rangle^{1/2} \simeq 4.16 \times 10^{-13} \text{ cm}$$

which compares well with the experimental value of 4.2×10^{-13} cm [Data quoted from Enge (1966); the value of a is suggested from the high energy experiments, see also Sachs (1953)].

PROBLEM 5.5

Consider the three-dimensional harmonic oscillator described by the potential energy function

$$V(x, y, z) = \frac{1}{2} m(\omega_1^2 x^2 + \omega_2^2 y^2 + \omega_3^2 z^2) \tag{70}$$

Using the method of separation of variables, solve the 3-dimensional Schrödinger equation and obtain the energy eigenvalues and the corresponding eigenfunctions. For an isotropic oscillator $\omega_1 = \omega_2 = \omega_3 = \omega$ (say) show that the energy eigenvalues are

$$\left(n + \frac{3}{2}\right)\hbar\omega$$

where $n = 0, 1, 2, \ldots.$ and for a particular value of n, the state is $\frac{1}{2}(n+1) \times (n+2)$ fold degenerate.

---

*The potential function described by Eq. (69) is known as the 'hard core' potential according to which the two particles cannot get closer than a certain distance a. This type of potential is indeed suggested by scattering experiments. It may be mentioned that the actual potential energy function describing nuclear forces is very complicated but many low energy phenomena are rather insensitive to the form of potential energy function and are reasonably well described by a short range attractive force of the type given by Eq. (69). For more details see Sachs (1953), Chapters 2 and 3.

PROBLEM 5.6

For an isotropic 3-dimensional harmonic oscillator solve the Schrödinger equation in spherical polar coordinates and show that the final result is consistent with the findings of Problem 5.5.

(*Hint:* In the radial part of the equation make the transformations

$$R(\xi) = \exp(-\xi/2)\xi^{l/2}F(\xi) \quad \text{with} \quad \xi = (m\omega/\hbar)r^2$$

and show that $F(\xi)$ satisfies the confluent hypergeometric equation (see Appendix G). In order to satisfy the boundary conditions, the series has to be terminated which gives the eigenvalues of the problem.)

PROBLEM 5.7

Consider the spherically symmetric potential well

$$V(r) = -V_0 \exp(-r/a) \tag{71}$$

For $l = 0$, solve the Schrödinger equation by making the following transformation

$$\xi = \exp(-r/2a) \tag{72}$$

which will transform Eq. (21) into a Bessel's equation. [see also Problem 12.3].

PROBLEM 5.8

Solve the Schrödinger equation for the following spherically symmetric potential energy function

$$V(r) = A/r^2 - B/r \qquad (A > 0, \quad B > 0) \tag{73}$$

and show that the energy levels are given by

$$E_p = -\frac{2B^2\mu}{\hbar^2}\left[(2p+1) + \left\{(2l+1)^2 + \frac{8\mu A}{\hbar^2}\right\}^{1/2}\right]^{-2} \tag{74}$$

where $p = 0, 1, 2, \ldots$. Positive values of E correspond to the continuum and negative values correspond to the discrete spectrum.

(*Hint:* As in the hydrogen atom problem, introduce the variable $\rho = (-8\mu E/\hbar^2)^{1/2}r$ and set

$$g(g+1) = l(l+1) + \frac{2\mu A}{\hbar^2}$$

The resulting equation will be similar to the one obtained in the hydrogen atom problem.)

PROBLEM 5.9

Solve the Schrödinger equation for the following potential energy function

$$V(r) = \frac{A}{r^2} + Br^2 \; (A > 0, \quad B > 0) \tag{75}$$

and show that the energy levels are given by

$$E_p = \hbar\left(\frac{B}{2\mu}\right)^{1/2}\left[4p + 2 + \left\{(2l+1)^2 + \frac{8\mu A}{\hbar^2}\right\}^{1/2}\right]; \; p = 0,1,2,\ldots \tag{76}$$

(*Hint:* see Problem 5.6.)

PROBLEM 5.10

(a) In the simplest model of a rotating diatomic molecule*, it is assumed to be a rigid rotator, i.e., the distance between the two atoms is assumed to be fixed. Show from classical considerations, that the rotational energy of such a rigid rotator is given by

$$\frac{L^2}{2\mu r_e^2}$$

where μ represents the reduced mass, r_e the distance between the two atoms (assumed to be fixed) and L represents the angular momentum of the molecule about the axis passing through the centre of mass. Obtain the quantized rotational energy levels.

(b) Molecules like HCl, HF, LiH can be considered as rigid rotators and because these molecules have permanent dipole moments, transitions take place only between adjacent rotational energy levels (this is the selection rule). Show that this leads to equally spaced lines in the emission as well as in the absorption spectra.

(c) The rotational absorption spectrum of HCl appears at wavenumbers 21.18, 42.36, 63.54, 84.72 and 105.91 cm^{-1}. Show that $R_0 \approx 1.3$ Å; assume $M_{Cl} \simeq 35M_H$ and $M_H \simeq 1.68 \times 10^{-24}$ g. It may be mentioned that these lines correspond to the far-infrared region where frequencies can be measured with great accuracy; as such the accuracy in the determination of R_0 is limited on account of the validity of the simple rigid rotator theory rather than the accuracy in the measurement of positions of the spectral lines.

PROBLEM 5.11

(a) In the previous problem we had neglected the vibrational motion of the diatomic molecule. In the simplest model describing the vibrational motion, the potential energy function corresponds to a Hooke's law type of interaction and is given by:

$$V(r) = \frac{1}{2} k(r - r_e)^2 \tag{77}$$

where k is the force constant and r_e the equilibrium distance. Assuming vibrations of small amplitude solve the Schrödinger equation to obtain the vibration-rotation spectra of diatomic molecules.

(b) The molecule HCl is known to give a single intense line at 2885.9 cm^{-1}. Assuming that vibrational transitions take place between adjacent levels, show that $k \approx 4.8 \times 10^5$ dynes/cm.

(c) Discuss the simultaneous rotation-vibration spectra.

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*A nice elementary account of diatomic molecular spectra has been given by Dunford (1968).

SOLUTIONS

SOLUTION 5.1

For $0 < r < a$, the radial part of the Schrödinger equation can be written in the form [see Eq. (19) for $V = 0$)

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[1 - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0 \tag{78}$$

where $\rho = kr$, $k = [2mE/\hbar^2]^{1/2}$. The solutions of the above equation are the spherical Bessel functions and the spherical Neumann functions (see Appendix H):

$$R(\rho) = Aj_l(\rho) + Bn_l(\rho) \tag{79}$$

Since $n_l(\rho)$ diverges at $\rho = 0$ (see Appendix H) we must set $B = 0$. Further, since the potential well is infinitely deep, $R(\rho)$ must vanish at $r = a$. Thus the transcendental equation which determines the energy eigenvalues is

$$j_l(ka) = 0 \tag{80}$$

Now $j_0(\rho) = \dfrac{\sin \rho}{\rho}$; thus for $l = 0$, Eq. (80) gives

$$ka = n\pi$$

or

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{81}$$

For $l = 1$ one obtains the equation

$$\tan ka = ka \tag{82}$$

which determines the energy eigenvalues. Similarly one can obtain the transcendental equations (determining the energy eigenvalues) for higher values of l.

SOLUTION 5.2

The Schrödinger equation is

$$\nabla^2\psi + \frac{2mE}{\hbar^2}\psi = 0 \qquad \begin{matrix} 0 < x < L \\ 0 < y < L \\ 0 < z < L \end{matrix} \tag{83}$$

with the boundary condition that ψ should vanish everywhere on the surface of the cube. We use the method of separation of variables and write $\psi = X(x)\,Y(y)\,Z(z)$ to obtain

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{2mE}{\hbar^2} \tag{84}$$

The first term is a function of x alone, the second term of y alone, etc., so that each term has to be set equal to a constant. We write

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k_x^2 \tag{85}$$

and similar equations for $Y(y)$ and $Z(z)$ with

$$k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2} \tag{86}$$

We have set each term equal to a negative constant; otherwise the boundary conditions cannot be satisfied. The solution of Eq. (85) is

$$X(x) = A \sin k_x x + B \cos k_x x \tag{87}$$

and since ψ has to vanish on all points on the surfaces $x = 0$ and $x = L$ we must have $B = 0$ and $k_x = n_x \pi / L$ with $n_x = 1, 2, \ldots$ (cf. Sec. 3.4.1). Similarly for k_y and k_z. Using Eq. (87) we get

$$E = \frac{\pi^2 \hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2); \quad n_x, n_y, n_z = 1, 2, 3, \ldots. \tag{88}$$

The corresponding normalized wavefunctions are

$$\psi = \left(\frac{8}{L^3}\right)^{1/2} \sin \frac{n_x \pi}{L} x \quad \sin \frac{n_y \pi}{L} y \quad \sin \frac{n_z \pi}{L} z \tag{89}$$

SOLUTION 5.3

In order to calculate the density of states $g(E)$ we first calculate $N(E)$ which represents the total number of states whose energies are less than E. Obviously

$$N(E) = \int_0^E g(E)\, dE \tag{90}$$

and therefore

$$g(E) = \frac{dN(E)}{dE} \tag{91}$$

Now,

$$n_x^2 + n_y^2 + n_z^2 = \frac{2mL^2 E}{\pi^2 \hbar^2} = R^2 \text{ (say)} \tag{92}$$

Thus $N(E)$ will be the number of sets of integers whose sum of the squares is less than R^2. In the n_x, n_y, n_z space each point corresponds to an unit volume and if we draw a sphere of radius R then the volume of the positive octant will approximately represent* $N(E)$; we have to take the positive octant because n_x, n_y and n_z take positive values. Thus

$$N(E) = 2 \times \frac{1}{8} \times \frac{4\pi}{3} R^3 = \frac{(2m)^{3/2} L^3}{3\pi^2 \hbar^3} E^{3/2} \tag{93}$$

*If the reader finds it difficult to understand he may first try to make the corresponding 2-dimensional calculations in which one is interested in finding the number of sets of integers such that $n_x^2 + n_y^2 < R^2$. If one takes a graph paper then each corner corresponds to a set of integers and each point can be associated with an unit area. Thus the number of sets of integers would be $1/4\, \pi R^2$ where the factor $1/4$ is because of the fact that we are interested in the positive quadrant.

where an additional factor of 2 has been introduced as a state can be occupied by 2 electrons. Using Eq. (91) we get Eq. (65).

(b) At $T = 0$,

$$\begin{aligned} F(E) &= 1 \qquad \text{for} \quad E < E_F \\ &= 0 \qquad \text{for} \quad E > E_F \end{aligned} \tag{94}$$

Thus

$$N = \int_0^\infty g(E)\,F(E)\,dE = \int_0^{E_{F_0}} g(E)\,dE = \frac{(2m)^{3/2}\,V}{3\pi^2\hbar^3}\,E_{F_0}{}^{3/2} \tag{95}$$

which gives Eq. (67). For metals like Na, Cu, etc. $E_{F_0} \approx$ few eV, which is much greater than $kT(\approx 1/40$ eV for $T \approx 300°\text{K})$. Thus $E_{F_0}/kT \gg 1$. Now, for $T \neq 0$

$$N = \int_0^\infty g(E)\,F(E)\,dE = \frac{(2m)^{3/2}V}{2\pi^2\hbar^3}\left[\frac{2}{3}\,E^{3/2}\,F(E)\Big|_0^\infty - \frac{2}{3}\int_0^\infty E^{3/2}\frac{dF}{dE}\,dE\right]$$

$$= -\frac{(2m)^{3/2}\,VE_F{}^{3/2}}{3\pi^2\hbar^3}\int_{-E_F/kT}^{\infty}\left(1+\frac{xkT}{E_F}\right)^{3/2}\frac{dF}{dx}\,dx \tag{96}$$

where $x = (E - E_F)/kT$. Assuming $E_F/kT \gg 1$ and since dF/dx is very sharply peaked around $x = 0$, we replace the lower limit by $-\infty$, expand $(1 + xkT/E_F)^{3/2}$ in a binomial series and integrate term by term to obtain*

$$N = -\frac{(2m)^{3/2}\,VE_F{}^{3/2}}{3\pi^2\hbar^3}\left[\Big[F(x)\Big]_{-\infty}^{+\infty} + 0 - \frac{3}{8}\left(\frac{kT}{E_F}\right)^2\int_{-\infty}^{+\infty}\frac{x^2e^x\,dx}{(1+e^x)^2} + \ldots\ldots\right]$$

$$\simeq \frac{(2m)^{3/2}\,VE_F{}^{3/2}}{3\pi^2\hbar^3}\left[1 + \frac{\pi^2}{8}\left(\frac{kT}{E_F}\right)^2\right] \tag{97}$$

Thus

$$E_F(T) \simeq E_{F_0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F0}}\right)^2 + \ldots\right] \tag{98}$$

---

*
$$\int_{-\infty}^{\infty}\frac{x^2e^x}{(1+e^x)^2}\,dx = 2\int_0^\infty x^2e^{-x}(1+e^{-x})^{-2}\,dx$$

$$= 2\left[\int_0^\infty x^2(e^{-x} - 2e^{-2x} + \cdots)\,dx\right]$$

$$= 4\left[1 - \frac{1}{2^2} + \frac{1}{3^2} - \cdots\right] = \pi^2/3$$

Similarly

$$\langle E\rangle = \int_0^\infty Eg(E)\, F(E)dE \simeq -\frac{(2m)^{3/2}\, VE_F{}^{5/2}}{3\pi^2\hbar^3}\int_{-\infty}^{\infty}\left(1+\frac{xkT}{E_F}\right)^{5/2} F(x)dx \tag{99}$$

from which we get

$$\langle E\rangle \simeq \frac{3}{5}\, nE_{F_0}\left[1+\frac{5\pi^2}{12}\left(\frac{kT}{E_{F_0}}\right)^2+\dots\right] \tag{100}$$

and

$$(c_v)_{\text{electronic}} = \frac{d}{dT}\Big(\langle E\rangle\Big) = \frac{3nk}{2}\left(\frac{\pi^2 kT}{3E_{F_0}}\right) \tag{101}$$

where $3nk/2$ represents the classical expression for the specific heat of the electron gas. For sodium metal $E_{F_0} \approx 3$eV and for $T \approx 300$°K, $kT \approx 1/40$ eV and the quantity inside the brackets is about 1/40.

(c) For sodium

$$n = \frac{6.023\times 10^{23}\times 0.97}{23} \simeq 2.54\times 10^{22}\ \text{electrons/cm}^3$$

Thus

$$E_{F_0} = \frac{(1.055\times 10^{-27})^2}{2\times 9.11\times 10^{-28}}\,(3\pi^2\times 2.54\times 10^{22})\ \text{ergs} \simeq 3.2\ \text{eV} \tag{102}$$

SOLUTION 5.4

The solution of Eq. (21) for $l = 0$ and $V(r)$ given by Eq. (69) is very straightforward. The boundary conditions are $u(r = a) = 0 = u(r = \infty)$. The continuity conditions give

$$\cot kb = -K/k = -\left[\frac{|E|}{V_0-|E|}\right]^{1/2} \simeq -0.2427 \tag{103}$$

where $k^2 = 2\mu(V_0-|E|)/\hbar^2$, $k^2 = 2\mu|E|/\hbar^2$, μ being the reduced mass. The lowest value of b will correspond to the ground state. Further

$$\langle r^2\rangle = \int_0^\infty r^2\,|u(r)|^2\, dr = A^2\int_a^{a+b} r^2\sin^2 k(r-a)\, dr + B^2\int_{a+b}^{\infty} r^2\exp(-2kr)\, dr$$

with

$$A = \left[\frac{2K}{1+Kb}\right]^{1/2} \text{ and } B = A\exp\,[K(a+b)]\sin kb$$

SOLUTION 5.5

Using the method of separation of variables, i.e., writing $\psi = X(x)\, Y(y)\, Z(z)$

we get

$$-\frac{\hbar^2}{2m}\,\frac{1}{X}\,\frac{dX}{dx^2}+\frac{1}{2}\,m\omega_1^2x_1^2=E_1 \tag{104}$$

and similar equations for $Y(y)$ and $Z(z)$. The above equation is the same as Eq. (49) of Chapter 3 and therefore

$$\begin{aligned}E &= E_1+E_2+E_3\\ &= (n_1+\tfrac{1}{2})\,\hbar\omega_1+(n_2+\tfrac{1}{2})\,\hbar\omega_2+(n_3+\tfrac{1}{2})\,\hbar\omega_3\end{aligned} \tag{105}$$

where $n_1, n_2, n_3 = 0, 1, 2, 3, \ldots$. The corresponding normalized wavefunctions are

$$\psi_{n_1n_2n_3}=\left(\frac{1}{2^n n_1!\,n_2!\,n_3!\,\pi^{3/2}}\right)^{1/2}H_{n_1}(\xi)\,H_{n_2}(\eta)\,H_{n_3}(\zeta)\exp\left(-\frac{\rho^2}{2}\right) \tag{106}$$

where

$$n=n_1+n_2+n_3,$$

$$\xi=\left(\frac{m\omega_1}{\hbar}\right)^{1/2}x,\ \eta=\left(\frac{m\omega_2}{\hbar}\right)^{1/2}y,\ \zeta=\left(\frac{m\omega_3}{\hbar}\right)^{1/2}z \tag{107}$$

and

$$\rho^2=\xi^2+\eta^2+\zeta^2$$

For an isotropic oscillator $\omega_1=\omega_2=\omega_3=\omega$ giving

$$E=\left(n+\frac{3}{2}\right)\hbar\omega \tag{108}$$

The degree of degeneracy is

$$(n+1)+n+(n-1)+\ldots+1=(n+1)(n+2)/2$$

SOLUTION 5.6

If we define $\xi=(m\omega/\hbar)r^2$ and*

$$R(\xi)=\exp\left(-\xi/2\right)\sum_r a_r\xi^{r+s} \tag{109}$$

the indicial equation gives $s=l/2$. The other root gives a negative value of s. The recurrence relation immediately gives

$$\begin{aligned}R(\xi) &= \exp\left(-\xi/2\right)\xi^{l/2}\left[1+\frac{a}{c}\,\frac{\xi}{1!}+\frac{a(a+1)}{c(c+1)}\,\frac{\xi^2}{2!}\right.\\ &\qquad\left.+\frac{a(a+1)\,(a+2)}{c(c+1)\,(c+2)}\,\frac{\xi^3}{3!}+\cdots\right]\\ &= \exp\left(-\xi/2\right)\xi^{l/2}\,{}_1F_1\,(a,c,\xi)\end{aligned} \tag{110}$$

---

*$R(\xi)$ satisfies the equation

$$\xi\,\frac{d^2R}{d\xi^2}+\frac{3}{2}\,\frac{dR}{d\xi}+\left[\frac{E}{2\hbar\omega}-\frac{l(l+1)}{4\xi}-\frac{\xi}{4}\right]R(\xi)=0$$

the asymptotic forms of the solution is obviously $\exp(\pm\,\xi/2)$ which suggests Eq. (109).

where ${}_1F_1\,(a, c, \xi)$ is the confluent hypergeometric function (see Appendix G) and

$$a = -\frac{E}{2\hbar\omega} + \frac{l}{2} + \frac{3}{2}\,, \; c = l/2$$

The series has to be terminated, otherwise it will behave as exp (ξ) as $\xi \to \infty$; thus we must have a $= 0, -1, -2, \ldots$ which gives

$$E = \hbar\omega\left[l + 2q + \frac{3}{2}\right];\; q = 0, 1, 2, \ldots \tag{111}$$

The normalized wavefunctions are

$$\psi(r, \theta, \varphi) = N \exp\left(-\frac{m\omega r^2}{2\hbar}\right) r^l\, {}_1F_1\left(-q, l + \frac{3}{2}, \frac{m\omega}{\hbar} r^2\right) \tag{112}$$

where

$$N = \left[\frac{2}{\Gamma(l + 3/2)}\right]^{1/2} \left(\frac{m\omega}{\hbar}\right)^{\frac{l}{2} + \frac{3}{4}} \text{ for } q = 0$$

$$= 2^{1/2}\left[\frac{(l + \frac{3}{2})\,(l + \frac{5}{2}) \ldots . (l + q + \frac{1}{2})}{\Gamma(l + 3/2)\, q!}\right]^{1/2} \left(\frac{m\omega}{\hbar}\right)^{\frac{l}{2} + \frac{3}{4}}$$

$$\text{for } q = 1, 2, \ldots$$

SOLUTION 5.7

The transformation $\xi = \exp\,(-r/2a)$ transforms Eq. (21) into the Bessel's equation, the solution of which (not diverging at $\xi = 0$ or $r = \infty$) is

$$u(\xi) = A\, J_\nu(g\xi) \tag{113}$$

where

$$\nu = \left[-\frac{8m\,Ea^2}{\hbar^2}\right]^{1/2} \text{ and } g = \left[\frac{8m\,V_0a^2}{\hbar^2}\right]^{1/2}$$

The condition that $u(r = 0) = 0$ gives

$$J_\nu(g) = 0 \tag{114}$$

which determines the energy eigenvalues. It may be mentioned that for $g < 2.405$ [the first zero of $J_0(x)$] there is no root of Eq. (114) and consequently no discrete mode exists. Numerical calculations for the deuteron problem are given in Solution 12.3.

SOLUTION 5.10

The rotational kinetic energy is $\frac{1}{2}\,I\omega^2$, where $I(= \mu r^2)$ is the moment of inertia about the axis passing through the centre of mass and μ the reduced mass. Further the angular momentum $L = I\omega$. Thus

$$\text{Rotational kinetic energy} = \frac{L^2}{2I} = \frac{L^2}{2\mu r_e^2} \tag{115}$$

Using Eq. (52) of Chapter 6, we get the following expression for the rotational energy levels

$$E = \frac{J(J+1)\hbar^2}{2\mu r_e^2} \tag{116}$$

where $J(= 0, 1, 2, \ldots .)$ is known as the rotational quantum number. For emission $J_f = J_i - 1$ (f and i refer to final and initial states) and the wavenumber of the emitted radiation is given by

$$\nu(\text{cm}^{-1}) = \frac{E_i - E_f}{hc} = 2J_iB \tag{117}$$

where $B = h/8\pi^2\mu r_e^2$ is known as the rotational constant. Thus the lines are equaly spaced. Similarly for absorption $J_f = J_i + 1$

$$\nu(\text{cm}^{-1}) = \frac{E_f - E_i}{hc} = 2(J_i + 1)\,B \tag{118}$$

SOLUTION 5.11

Equation (21) for $V(r)$ given by Eq. (77) can be written in the form

$$\frac{d^2u}{d\rho^2} + \frac{2\mu}{\hbar^2}\left[E - \frac{J(J+1)\hbar^2}{2\mu(r_e+\rho)^2} - \frac{1}{2}k\rho^2\right]u(\rho) = 0 \tag{119}$$

where we have written $J(J+1)$ instead of $l(l+1)$ (so as to be consistent with the spectroscopic notation) and $\rho = r - r_e$. Now for small vibrations we may neglect ρ in the denominator so that Eq. (119) becomes

$$\frac{d^2u}{d\rho^2} + \frac{2\mu}{\hbar^2}\left[E - \frac{J(J+1)\hbar^2}{2\mu r_e^2} - \frac{1}{2}k\rho^2\right]u(\rho) = 0 \tag{120}$$

with the boundary condition that $u(r=0) = 0 = u(r=\infty)$ which gives $u(\rho = -r_e) = 0 = u(\rho = \infty)$. We may consider this approximately equivalent to $u(\rho = -\infty) = 0 = u(\rho = \infty)$. Thus Eq. (120) and the boundary conditions are equivalent to the one dimensional oscillator problem so that we may write

$$E = E\text{rot} + E\text{vib} \tag{121}$$

where

$$E\text{rot} = \frac{J(J+1)\hbar^2}{2\mu r_e^2} \tag{122}$$

and

$$E\text{vib} = \left(v + \frac{1}{2}\right)\hbar\sqrt{k/\mu} \tag{123}$$

represent the rotational and vibrational energies respectively. If we neglect Erot then transition between adjacent vibration levels will give rise to a line of wavenumber

$$\nu(\text{cm}^{-1}) = \frac{E(v+1) - E(v)}{hc} = \frac{1}{2\pi c}\sqrt{k/\mu} \tag{124}$$

from which we can determine the value of k. For a simultaneous vibrational and rotational transition the selection rules are

$$\begin{aligned} v_f &= v_i + 1, \qquad & J_f &= J_i + 1 \\ v_f &= v_i + 1, & J_f &= J_i - 1 \\ v_f &= v_i - 1, & J_f &= J_i + 1 \\ v_f &= v_i - 1, & J_f &= J_i - 1 \end{aligned} \tag{125}$$

and since, in general, $(1/2\pi c)\sqrt{k/\mu} \gg B$ the first two selection rules correspond to absorption and the last two to emission.

It is of interest to mention that in a more accurate analysis we write

$$\begin{aligned} E - \frac{J(J+1)\hbar^2}{2\mu(r_e+\rho)^2} = \frac{1}{2}k\rho^2 &\simeq E - \frac{J(J+1)\hbar^2}{2\mu r_e^2}\left(1 - \frac{2\rho}{r_e} + \frac{3\rho^2}{r_e^2}\right) \\ -\frac{1}{2}k\rho^2 &\simeq \left[E - E\text{rot} + \frac{\overset{2}{E}\text{rot}}{3E\text{rot} + \frac{1}{2}kr_e^2}\right] \\ &\qquad - \left(\frac{1}{2}k + \frac{3E\text{rot}}{r_e^2}\right)\xi^2 \end{aligned} \tag{126}$$

where $\xi = \rho - \dfrac{E\text{rot}\, r_e}{3E\text{rot} + \frac{1}{2}kr_e^2}$. Thus a more accurate expression for the energy eigenvalues is

$$E = E\text{rot} + \frac{\overset{2}{E}\text{rot}}{3E\text{rot} + \frac{1}{2}kr_e^2} + \left[v + \frac{1}{2}\right]\hbar\sqrt{\left(k + \frac{6E\text{rot}}{r_e^2}\right)\Big/\mu} \tag{127}$$

CHAPTER SIX

Angular Momentum : I

6.1 Introduction

The theory of angular momentum occupies a very important place in the study of quantum mechanics because of its application in numerous problems of physical interest. The basic theory of angular momentum will be developed in this chapter as well as in Chapter 9.

In Sec. 6.2 we will define the angular momentum operator through the classical relation $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and replace $\mathbf{p}$ by its operator representation $-i\hbar\nabla$. We will then consider the representations of the cartesian components of the angular momentum operator in spherical polar co-ordinates and solve the eigenvalue equations for L^2 and L_z. In Sec. 6.5 the commutation relations between L_x, L_y and L_z will be derived which will be the starting equations in Chapter 9. The relationship of angular momentum with rotations will be discussed in Sec. 6.6. In the remaining sections, certain important characteristics of the angular momentum operator will be discussed.

6.2 The Angular Momentum Operators and their Representation in Spherical Polar Co-ordinates

In classical mechanics the angular momentum of a particle is defined through the relation

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{1}$$

where $\mathbf{r}$ and $\mathbf{p}$ represent the position and linear momentum of the particle. Thus

$$L_x = yp_z - zp_y \tag{2}$$

with similar relations for L_y and L_z. In quantum mechanics we replace p_x, p_y and p_z by the corresponding operators [see Eq. (19) of Chapter 2] to obtain the following operator representations of L_x, L_y and L_z

$$\left.\begin{aligned} L_x &= yp_z - zp_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ L_y &= zp_x - xp_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ L_z &= xp_y - yp_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned}\right\} \tag{3}$$

In order to determine the eigenvalues and eigenfunctions of the operator $L^2 (\equiv L_x^2 + L_y^2 + L_z^2)$ it is convenient to express L_x, L_y and L_z in spherical polar co-ordinates which are defined through the following equations (see Fig. 6.1)

$$x = r \sin\theta \cos\varphi \tag{4}$$

$$y = r \sin\theta \sin\varphi \tag{5}$$

$$z = r \cos\theta \tag{6}$$

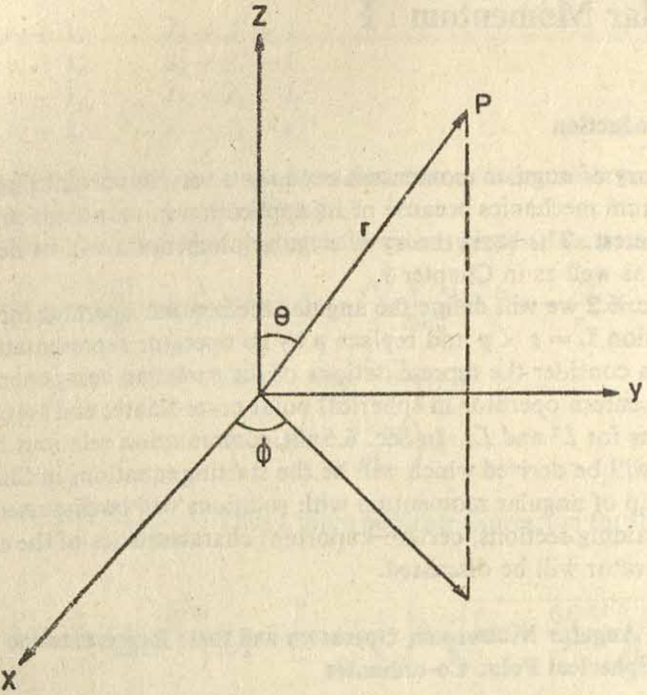

Fig. 6.1. The definition of spherical polar co-ordinates.

Thus

$$r^2 = x^2 + y^2 + z^2 \tag{7}$$

$$\tan^2 \theta = \frac{(x^2 + y^2)}{z^2} \tag{8}$$

$$\tan \varphi = \frac{y}{x} \tag{9}$$

Now*

$$2r \frac{\partial r}{\partial x} = 2x \tag{10}$$

$$2 \tan \theta \sec^2 \theta \ \frac{\partial \theta}{\partial x} = \frac{2x}{z^2} = \frac{2}{r} \tan \theta \sec \theta \cos \varphi \tag{11}$$

$$\sec^2 \varphi \frac{\partial \varphi}{\partial x} = -\frac{y}{x^2} = -\frac{1}{r} \operatorname{cosec} \theta \sec \varphi \tan \varphi \tag{12}$$

---

*Notice that $\frac{\partial x}{\partial r} = \sin \theta \cos \varphi = \frac{x}{r}$. Thus $\left(\frac{\partial r}{\partial x}\right) \neq 1 \Big/ \left(\frac{\partial x}{\partial r}\right)$

giving

$$\frac{\partial r}{\partial x} = \sin\theta\cos\varphi \tag{13}$$

$$\frac{\partial\theta}{\partial x} = \frac{1}{r}\cos\theta\cos\varphi \tag{14}$$

$$\frac{\partial\varphi}{\partial x} = -\frac{1}{r}\sin\varphi\,\mathrm{cosec}\,\theta \tag{15}$$

Similarly we can obtain $\partial r/\partial y$, $\partial\theta/\partial y$, etc. Now

$$\begin{aligned}
L_z\psi(r,\theta,\varphi) &= -i\hbar\left[x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x}\right]\\
&= -i\hbar\left[x\left(\frac{\partial\psi}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial y} + \frac{\partial\psi}{\partial\varphi}\frac{\partial\varphi}{\partial y}\right)\right.\\
&\qquad\left. - y\left(\frac{\partial\psi}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial x} + \frac{\partial\psi}{\partial\varphi}\frac{\partial\varphi}{\partial x}\right)\right]\\
&= -i\hbar\left[r\sin\theta\cos\varphi\left\{\frac{\partial\psi}{\partial r}\left(\sin\theta\sin\varphi\right)\right.\right.\\
&\qquad\left. + \frac{\partial\psi}{\partial\theta}\left(\frac{1}{r}\cos\theta\sin\varphi\right) + \frac{\partial\psi}{\partial\varphi}\left(\frac{1}{r}\cos\varphi\,\mathrm{cosec}\,\theta\right)\right\}\\
&\qquad - r\sin\theta\sin\varphi\left\{\frac{\partial\psi}{\partial r}\left(\sin\theta\cos\varphi\right) + \frac{\partial\psi}{\partial\theta}\left(\frac{1}{r}\cos\theta\cos\varphi\right)\right.\\
&\qquad\left.\left. + \frac{\partial\psi}{\partial\varphi}\left(-\frac{1}{r}\sin\varphi\,\mathrm{cosec}\,\theta\right)\right\}\right]
\end{aligned}$$

or

$$L_z\,\psi(r,\theta,\varphi) = -i\hbar\,\frac{\partial}{\partial\varphi}\,\psi(r,\theta,\varphi) \tag{16}$$

Since the above equation holds for arbitrary $\psi(r, \theta, \varphi)$, we have the following operator representation for L_z

$$L_z = -i\hbar\,\frac{\partial}{\partial\varphi} \tag{17}$$

Similarly (see also Problem 6.3)

$$L_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) \tag{18}$$

$$L_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right) \tag{19}$$

The operator L^2 is defined through the following equation

$$L^2 = L_x^2 + L_y^2 + L_z^2 \tag{20}$$

where the square of an operator is defined by

$L_x^2 = L_x L_x$ etc.

Thus

$$L_z^2\,\psi(r,\theta,\varphi) = L_z L_z \psi = (-i\hbar)^2 \frac{\partial}{\partial\varphi}\frac{\partial}{\partial\varphi}\psi = -\hbar^2 \frac{\partial^2}{\partial\varphi^2}\psi$$

Hence, the operator representation of L_z^2 is given by

$$L_z^2 = -\hbar^2 \frac{\partial^2}{\partial\varphi^2} \tag{21}$$

Similarly we can obtain the operator representations of L_x^2 and L_y^2 (although the algebra is much more involved). Adding up, we get (see also Problem 6.5)

$$L^2 = -\hbar^2 \left\{ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \right\} \tag{22}$$

It may be noted that (see Problem 6.6)

$$L^2 = -\hbar^2 r^2 \left\{ \nabla^2 - \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right\} \tag{23}$$

6.3 Eigenvalues and Eigenfunctions of $\mathbf{L}^2$

The eigenvalues and eigenfunctions of L^2 play an extremely important role in quantum mechanics (see, e.g. Sec. 5.2). In this section we will solve the eigenvalue equation

$$L^2 Y(\theta,\varphi) = \lambda\hbar^2\, Y(\theta,\varphi) \tag{24}$$

where $\lambda\hbar^2$ represents the eigenvalues of L^2 and $Y(\theta,\varphi)$ the corresponding eigenfunctions. We will show that λ takes the values $l(l+1)$ where $l = 0, 1, 2, \ldots$ and the corresponding eigenfunctions are the spherical harmonics. For each value of l there will be $(2l+1)$ fold degeneracy; i.e., there will be $(2l+1)$ eigenfunctions belonging to the same eigenvalue $l(l+1)\hbar^2$.

Now, substituting for L^2 from Eq. (22) in Eq. (24), we obtain

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} + \lambda Y(\theta,\varphi) = 0 \tag{25}$$

In order to solve the above equation, we try the method of separation of variables and write

$$Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi) \tag{26}$$

On substitution and subsequent multiplication by $\sin^2\theta/Y(\theta,\varphi)$ we obtain

$$\frac{\sin^2\theta}{\Theta}\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \lambda\,\Theta(\theta)\right] = -\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = m^2 \tag{27}$$

The variables have indeed separated out and we have set each side equal to a *positive* constant m^2, the reason for setting equal to a positive constant will shortly become clear. Equation (27) gives us

$$\frac{d^2\Phi}{d\varphi^2} + m^2\,\Phi(\varphi) = 0$$

the solution of which is given by

$$\Phi(\varphi) \sim e^{im\varphi}$$

For the wavefunction to be single valued, we must have

$$\Phi(\varphi + 2\pi) = \Phi(\varphi) \tag{28}$$

or

$$e^{2\pi m i} = 1$$

giving*

$$m = 0, \pm 1, \pm 2, \ldots .$$

We label the functions by the subscript m

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}; \quad m = 0, \pm 1, \pm 2, \ldots \tag{29}$$

where the factor $\frac{1}{\sqrt{2\pi}}$ ensures that

$$\int_0^{2\pi} |\Phi_m(\varphi)|^2 \, d\varphi = 1$$

Indeed

$$\int_0^{2\pi} \Phi^*_{m'}(\varphi)\, \Phi_m(\varphi)\, d\varphi = \delta_{mm'} \tag{30}$$

The equation satisfied by $\Theta(\theta)$ is [from Eq. (27)]

$$\frac{1}{\sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta(\theta) = 0 \tag{31}$$

Writing $\cos\theta = \mu$ and $\Theta(\theta) = F(\mu)$, we obtain

$$\frac{d}{d\mu}\left[(1-\mu^2)\frac{dF}{d\mu}\right] + \left[\lambda - \frac{m^2}{1-\mu^2}\right]F(\mu) = 0 \tag{32}$$

We first consider the case $m = 0$ and then $m \neq 0$.

6.3.1 CASE I: $m = 0$

For $m = 0$, Eq. (32) reduces to

$$(1-\mu^2)\frac{d^2P}{d\mu^2} - 2\mu\frac{dP}{d\mu} + \lambda P(\mu) = 0 \tag{33}$$

---

*It immediately follows that we could not have set $1/\Phi\ (d^2\Phi/d\varphi^2)$ to a positive (or complex) constant for, then the wavefunction would not have been single valued.

where we have substituted $P(\mu)$ for $F(\mu)$. As in the case of the linear harmonic oscillator problem, we try a power series solution

$$P(\mu) = \sum_{r=0,1,\ldots}^{\infty} a_r \mu^{r+s} \tag{34}$$

Differentiating (34) term by term and substituting in (33), we obtain

$$\sum_{r=0}^{\infty} [(r+s)(r+s-1)\, a_r \mu^{r+s-2} - \{(r+s)(r+s-1) + 2(r+s) - \lambda\}\, a_r \mu^{r+s}] = 0$$

Since the above equation is to be valid for all values of μ, we equate the coefficients of each power of μ to zero. Thus

$$s(s-1)\, a_0 = 0 \tag{35}$$

$$s(s+1)\, a_1 = 0 \tag{36}$$

and

$$(r+s+2)(r+s+1)\, a_{r+2} = [(r+s)(r+s+1) - \lambda]\, a_r; \; r = 0, 1, 2 \ldots \tag{37}$$

The roots of the indicial equation [Eq. (35)] gives

$$s = 0 \quad \text{or} \quad s = 1 \tag{38}$$

For $s = 0$, the recurrence relation is*

$$\frac{a_{r+2}}{a_r} = \frac{r(r+1) - \lambda}{(r+1)(r+2)} \to 1 \qquad (\text{as } r \to \infty)$$

Thus, if the series does not terminate, it will diverge for values of $\mu = \pm 1$ (i.e., for $\theta = 0$ and π). However, for

$$\lambda = l(l+1); \quad l = 0, 1, 2 \ldots \tag{39}$$

the series will terminate at $a_l \mu^l$; this can easily be seen by writing Eq. (34) as

$$P(\mu) = a_0\left[1 + \frac{a_2}{a_0}\mu^2 + \frac{a_4}{a_0}\mu^4 + \ldots\right] + a_1\left[\mu + \frac{a_3}{a_1}\mu^3 + \frac{a_5}{a_1}\mu^5 + \ldots\right]$$

For example, for $l = 2$ the even series will terminate at μ^2 (because $a_4 = a_6 = \ldots = 0$); however, the odd series will not terminate and hence we must set $a_1 = 0$. Similarly, for an odd value of l the odd series will terminate at μ^l and to terminate the even series we must set $a_0 = 0$. The resulting polynomials are known as the Legendre polynomials $P_l(\mu)$. The first few Legendre polynomials are

$$P_0(\mu) = 1; \quad P_1(\mu) = \mu; \quad P_2(\mu) = \tfrac{1}{2}(3\mu^2 - 1) \text{ etc.} \tag{40}$$

---

*Since the root $s = 0$ makes a_1 indeterminate, it provides all the necessary independent solutions (see, e.g., Irving and Mullineux, 1961).

The Legendre polynomials satisfy the following relation

$$\int_{-1}^{+1} P_l(\mu)\, P_{l'}(\mu)\, d\mu = \frac{2}{2l+1}\, \delta_{ll'} \tag{41}$$

Thus the orthonormal set of solutions of Eqs. (32) and (25), for $m = 0$, are

$$\Theta_l(\theta) = \left(\frac{2l+1}{2}\right)^{1/2} P_l(\cos\theta)$$

and

$$Y_{l,\,0}(\theta, \varphi) = \frac{1}{\sqrt{2\pi}}\, \Theta_l(\theta) = \left(\frac{2l+1}{4\pi}\right)^{1/2} P_l(\cos\theta) \tag{42}$$

respectively. The subscripts of $Y(\theta, \varphi)$ represent the values of l and m. The orthonormality condition is

$$\iint Y_{l'0}\, Y_{l0} \sin\theta\, d\theta\, d\varphi = \left[\frac{1}{2\pi}\int_0^{2\pi} d\varphi\right]\left[\int_0^{\pi} \Theta_{l'}(\theta)\, \Theta_l(\theta)\, \sin\theta\, d\theta\right]$$
$$= \delta_{ll'} \tag{43}$$

6.3.2 CASE II: $m \neq 0$

We first consider *positive* values of m. Now, in order to obtain the solution of Eq. (32) for $m > 0$, we differentiate Eq. (33) m times to obtain

$$(1 - \mu^2)\frac{d^2P^{(m)}}{d\mu^2} - 2(m+1)\frac{dP^{(m)}}{d\mu} + [\lambda - m(m+1)]\, P^m(\mu) = 0 \tag{44}$$

where

$$P^{(m)}(\mu) = \frac{d^mP}{d\mu^m} \tag{45}$$

Further, in Eq. (32), if we make the substitution

$$F(\mu) = (1 - \mu^2)^{m/2}\, G(\mu) \tag{46}$$

then $G(\mu)$ will be found to satisfy the same equation as satisfied by $P^{(m)}$ [i.e., Eq. (44)]. Thus for $m = 1, 2, 3, \ldots$ the solution of Eq. (32) is the associated Legendre polynomial (see Appendix I)

$$P_l^m(\mu) = (1 - \mu^2)^{m/2}\, \frac{d^mP_l(\mu)}{d\mu^m} \tag{47}$$

defined only for non-negative integers. Since $P_l(\mu)$ is a polynomial of degree l, we must have $m \leqslant l$. Obviously,

$$P_l^0(\mu) = P_l(\mu)$$

Thus, the 'well-behaved' solutions of Eq. (25) are

$$Y_{lm}(\theta, \varphi) = (-1)^m\left[\frac{2l+1}{4\pi}\, \frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta)\, e^{im\varphi};\quad m \geqslant 0 \tag{48}$$

For negative values of m, Eq. (32) and therefore the part dependent on θ remains the same, only the φ dependent part changes. Thus, for $m < 0$, we may define the solution

$$Y_{lm}(\theta, \varphi) \equiv (-1)^m \, Y^*_{l,-m}(\theta, \varphi); \quad m < 0 \tag{49}$$

Further,

$$l = 0, 1, 2, \ldots . ; \quad m = -l, -l+1, \ldots . l-1, l \tag{50}$$

The constant factor* in Eq. (48) is such that

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta \, Y^*_{lm}(\theta, \varphi) \, Y_{l'm'}(\theta, \varphi) = \delta_{ll'} \, \delta_{mm'} \tag{51}$$

Thus the eigenvalue equation for L^2 [see Eq. (24)] takes the form

$$L^2 \, Y_{lm}(\theta, \varphi) = l(l+1)\hbar^2 \, Y_{lm}(\theta, \varphi) \tag{52}$$

where $l(l+1)\hbar^2$ (with $l = 0, 1, 2, \ldots$) represents the eigenvalues of L^2, $Y_{lm}(\theta, \varphi)$ being the corresponding eigenfunctions. Notice that the eigenvalue $l(l+1)\hbar^2$ is $(2l+1)$ fold degenerate; i.e., corresponding to a particular value of l there will be $(2l+1)$ values of m ($= -l, -l+1, \ldots, l-1, l$). Since the φ-dependence of $Y_{lm}(\theta, \varphi)$ is of the form $\exp(im\varphi)$, we obtain

$$L_z \, Y_{lm}(\theta, \varphi) = -i\hbar \frac{\partial}{\partial \varphi}\left[\Theta_l(\theta) \frac{1}{\sqrt{2\pi}} e^{im\varphi}\right]$$

or

$$L_z \, Y_{lm}(\theta, \varphi) = m\hbar \, Y_{lm}(\theta, \varphi) \tag{53}$$

where we have used Eq. (17). Thus $Y_{lm}(\theta, \varphi)$ are simultaneous eigenfunctions of L^2 and L_z. It is easy to show that they are not eigenfunctions of L_x and L_y except for the case $l = 0$, $m = 0$. In fact, it is impossible to construct eigenfunctions of any but L^2 and one** of the three components of **L**. This follows from the fact that L_x, L_y and L_z do not commute (see Sec. 6.5).

6.4 The Spherical Harmonics

The functions $Y_{lm}(\theta, \varphi)$ are known as spherical harmonics. In Appendix I we have given some of the properties of these functions. In this section we will just give the expressions for the first few spherical harmonics.

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*The choice of the constant factor is consistent with the definition of $Y_{lm}(\theta, \varphi)$ given by Condon and Shortley (1953), Blatt and Weisskopf (1952), etc.; however, it differs by a phase factor from the definition given by Schiff (1968).

**Once again, the case $l = 0$, $m = 0$ is an exception because $Y_{00}(\theta, \varphi)$ is a simultaneous eigenfunction of the operators L^2, L_x, L_y and L_z.

$l = 0: \qquad 2l + 1 = 1; \quad m = 0$

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \tag{54}$$

$l = 1: \qquad 2l + 1 = 3; \quad m = 1, 0, -1$

$$Y_{1,1} = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{i\varphi} \tag{55}$$

$$Y_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \tag{56}$$

$$Y_{1,-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{-i\varphi} \tag{57}$$

$l = 2: \qquad (2l + 1) = 5; \quad m = 2, 1, 0, -1, -2$

$$Y_{2,2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{2i\varphi} \tag{58}$$

$$Y_{2,1} = -\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta\, e^{i\varphi} \tag{59}$$

$$Y_{2,0} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \tag{60}$$

$$Y_{2,-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta\, e^{-i\varphi} \tag{61}$$

$$Y_{2,-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{-2i\varphi} \tag{62}$$

$l = 3: \qquad 2l + 1 = 7; \quad m = 3, 2, 1, 0, -1, -2, -3,$ etc.

6.5 The Commutation Relations

In this section we will show that the components of the angular momentum operator do not commute. For example,

$$\begin{aligned}
[L_x, L_y] &= L_xL_y - L_yL_x \\
&= (yp_z - zp_y)(xp_z - zp_x) - (xp_z - zp_x)(yp_z - zp_y) \\
&= yp_zxp_z - yp_zzp_x - zp_yxp_z + zp_yzp_x \\
&\quad - xp_zyp_z + zp_xyp_z + xp_zzp_y - zp_xzp_y \\
&= yp_x(zp_z - p_zz) - xp_y(zp_z - p_zz) \\
&= (yp_x - xp_y)\, i\hbar
\end{aligned}$$

or

$$[L_x, L_y] = i\hbar\, L_z \tag{63}$$

where we have used the commutation relations derived in Sec. 2.3. Similarly,

$$[L_y, L_z] = i\hbar\, L_x \tag{64}$$

$$[L_z, L_y] = i\hbar\, L_y \tag{65}$$

These commutation relations will be the starting point of Chapter 9 where we will show that if we just use these commutation relations then the angular momentum components can have values $0, \frac{1}{2}\hbar, \hbar, \frac{3}{2}\hbar, 2\hbar$, etc.* This existence of systems having components of angular momenta whose values are half integral multiplies of $\hbar$ leads to extremely important considerations. We will discuss these in Chapter 9.

6.6 Angular Momentum and Rotations

We now show that the angular momentum is related to the rotations of a system**. In fact, each component of $\mathbf{L}$ is related to an infinitesimal rotation about the corresponding axis. For example, the effect of a rotation about the z-axis through an infinitesimal angle $\Delta\alpha$ results in the following transformations (see Fig. 6.2)

$$\begin{aligned} x &= x' \cos(\Delta\alpha) - y' \sin(\Delta\alpha) \\ y &= x' \sin(\Delta\alpha) + y' \cos(\Delta\alpha) \\ z &= z' \end{aligned} \tag{66}$$

or

$$\begin{aligned} x' &= x \cos(\Delta\alpha) + y \sin(\Delta\alpha) \\ y' &= -x \sin(\Delta\alpha) + y \cos(\Delta\alpha) \\ z' &= z \end{aligned}$$

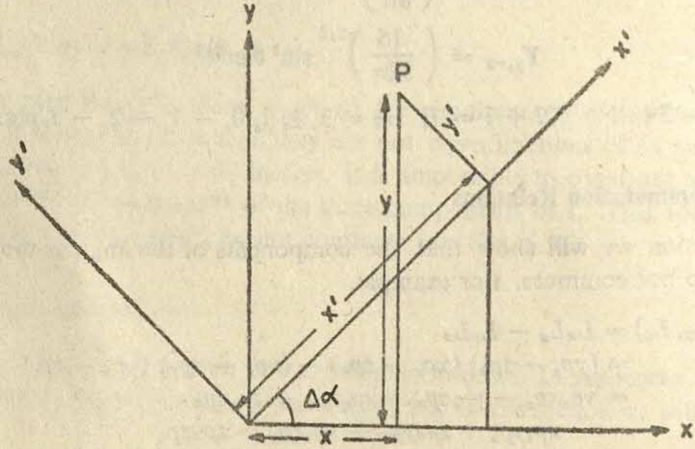

Fig. 6.2. Rotation about the z-axis by an angle $\Delta\alpha$.

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*It may be noted that in this chapter we have shown that components of angular momenta, defined as $\mathbf{r} \times \mathbf{p}$ can only have eigenvalues $0, \hbar, 2\hbar, \ldots$ etc.

**Later, we will show that if the system has rotational symmetry, then the eigenstates of the Hamiltonian will have well defined values of L^2.

Since $\Delta\alpha$ is infinitesimal, we may write

$$\begin{aligned} x' &= x + y\,\Delta\alpha \\ y' &= y - x\,\Delta\alpha \\ z' &= z \end{aligned} \tag{67}$$

Thus, if $R_z(\Delta\alpha)$ represents the rotational operator corresponding to a rotation about the z-axis through an infinitesimal angle $\Delta\alpha$, then the effect of this rotation on an arbitrary function ψ is given by

$$\begin{aligned} R_z(\Delta\alpha)\,\psi(x, y, z) &= \psi(x', y', z') \\ &= \psi(x + y\,\Delta\alpha,\, y - x\,\Delta\alpha,\, z) \\ &= \psi(x, y, z) + y\,\Delta\alpha\frac{\partial\psi}{\partial x} - x\Delta\alpha\frac{\partial\psi}{\partial y} \end{aligned}$$

where we have retained only the first term in the Taylor expansion because $\Delta\alpha$ is infinitesimal. Thus,

$$R_z(\Delta\alpha)\,\psi(x, y, z) = \left[1 + \Delta\alpha\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)\right]\psi(x, y, z)$$

But

$$L_z = xp_y - yp_x = i\hbar\left[y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right]$$

and since $\psi(x, y, z)$ is arbitrary we can write

$$R_z(\Delta\alpha) = 1 + \frac{\Delta\alpha}{i\hbar}L_z \tag{68}$$

Similarly,

$$R_x(\Delta\alpha) = 1 + \frac{\Delta\alpha}{i\hbar}L_x \tag{69}$$

and

$$R_y(\Delta\alpha) = 1 + \frac{\Delta\alpha}{i\hbar}L_y \tag{70}$$

The operators, L_x, L_y and L_z are called the *generators* of the infinitesimal rotations about the three co-ordinate axes.

In order to find $R_z(\alpha)$ for some *finite* rotation α about the z-axis, we note that the effect of a small increase in the magnitude of α, from α to $\alpha + \Delta\alpha$, is to follow the finite rotation $R_z(\alpha)$ by the infinitesimal rotation $R_z(\Delta\alpha)$ to give

$$R_z(\alpha + \Delta\alpha) = R_z(\Delta\alpha)\,R_z(\alpha) = \left[1 + \frac{1}{i\hbar}\Delta\alpha\,L_z\right]R_z(\alpha)$$

Thus

$$\frac{dR_z}{d\alpha} = \underset{\Delta\alpha\to 0}{\mathrm{Lt}}\;\frac{R_z(\alpha + \Delta\alpha) - R_z(\alpha)}{\Delta\alpha} = -\frac{i}{\hbar}L_z$$

The above equation can be integrated to give

$$R_z(\alpha) = \exp\left[-\frac{i}{\hbar}\alpha L_z\right] \tag{71}$$

where we have incorporated the boundary condition that $R_z(0) = 1$. It may be mentioned that the exponential of an operator has no meaning except as the infinite series given below

$$e^{\mathcal{O}} = 1 + \mathcal{O} + \frac{\mathcal{O}\mathcal{O}}{2!} + \frac{\mathcal{O}\mathcal{O}\mathcal{O}}{3!} + \ldots \tag{72}$$

Equations (68)-(70) can be used to obtain the differential operator representation of the components of the angular momentum operator in spherical polar co-ordinates [see Eqs. (17)-(19)]. For example, if we consider rotation about the z-axis through an infinitesimal angle $\Delta\alpha$, then, the transformations of the spherical polar co-ordinates are given by

$$r \to r, \quad \theta \to \theta, \quad \varphi \to \varphi - \Delta\alpha$$

$$\therefore \qquad R_z(\Delta\alpha)\,\psi(r, \theta, \varphi) = \psi(r, \theta, \varphi - \Delta\alpha)$$

or

$$\left[1 - \frac{i}{\hbar}(\Delta\alpha)\,L_z\right]\psi(r, \theta, \varphi) = \psi(r, \theta, \varphi) - \Delta\alpha\,\frac{\partial\psi}{\partial\varphi}$$

Since the above equation is valid for arbitrary ψ we obtain the following differential operator representation of L_z [see Eq. (17)]

$$L_z = -i\hbar\,\frac{\partial}{\partial\varphi} \tag{73}$$

Similarly, we can obtain the corresponding representations for L_x and L_y (see Problem 6.3).

6.7 Active and Passive Points of View

We next consider a more general case in which the wavefunction depends on n co-ordinates, as

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n)$$

and the infinitesimal rotation by an angle $\delta\varphi$ is about an arbitrary axis, the direction of which is denoted by the unit vector $\hat{\mathbf{n}}$. Under this rotation the co-ordinates $\mathbf{r}_j$ will all change. (Imagine the axis to be fixed, but the points $\mathbf{r}_j$ to move. This is called the *active point of view*. We could also consider that the axes are rotated by an angle $\delta\varphi$ about $\hat{\mathbf{n}}$ the *passive point of view*.) The new co-ordinates are

$$\mathbf{r}_j' = \mathbf{r}_j + \delta\,\mathbf{r}_j \tag{74}$$

where

$$\delta\mathbf{r}_j = \delta\varphi(\hat{\mathbf{n}} \times \mathbf{r}_j) \tag{75}$$

Thus the wave function is now to be evaluated at $\mathbf{r}_1 + \delta\mathbf{r}_1, \mathbf{r}_2 + \delta\mathbf{r}_2, \ldots\ldots, \mathbf{r}_n + \delta\mathbf{r}_n$ and will yield a *new* number,

$$\psi(\mathbf{r}_1 + \delta\mathbf{r}_1, \mathbf{r}_2 + \delta\mathbf{r}_2, \ldots\ldots, \mathbf{r}_n + \delta\mathbf{r}_n) \simeq \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n) + \sum_j (\nabla_j\psi)\cdot\delta\mathbf{r}_j \tag{76}$$

to first order in the $\delta\mathbf{r}_j$. From Eq. (75) we obtain for the change* in ψ

$$\begin{aligned}\psi(\mathbf{r}') - \psi(\mathbf{r}) &= \delta\varphi \sum_j (\hat{\mathbf{n}} \times \mathbf{r}_j)\cdot\nabla_j\psi \\ &= \delta\varphi \sum_j \hat{\mathbf{n}}\cdot(\mathbf{r}_j \times \nabla_j\psi) \\ &= \delta\varphi\, \hat{\mathbf{n}} \cdot \sum_j \mathbf{r}_j \times \nabla_j\psi\end{aligned} \tag{77}$$

where we have used the identity $(\mathbf{a}\times\mathbf{b})\cdot\mathbf{c} = \mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})$. If we define, as before,

$$\mathbf{l}_j = \mathbf{r}_j \times \mathbf{p}_j = -i\hbar\, \mathbf{r}_j \times \nabla_j \tag{78}$$

we obtain

$$\psi(\mathbf{r}') - \psi(\mathbf{r}) = \frac{i}{\hbar}\delta\varphi\,\hat{\mathbf{n}}\cdot\left(\sum_j \mathbf{l}_j\right)\psi \tag{79}$$

if we define the total (orbital) angular momentum of the system

$$\mathbf{L} = \sum_j \mathbf{l}_j \tag{80}$$

then

$$\psi(\mathbf{r}') - \psi(\mathbf{r}) = \frac{i}{\hbar}\delta\varphi\,\hat{\mathbf{n}}\cdot\mathbf{L}\,\psi \tag{81}$$

which could be written as

$$\psi(\mathbf{r}') = \left[1 + \frac{i}{\hbar}\delta\varphi\,\hat{\mathbf{n}}\cdot\mathbf{L}\right]\psi(\mathbf{r}) \tag{82}$$

For a finite rotation φ, built up by successive rotations $\delta\varphi$ (around the same axis!), it is easy to see that we shall obtain

$$\psi(\mathbf{r}') = \exp\left[\frac{i}{\hbar}\varphi\,\hat{\mathbf{n}}\cdot\mathbf{L}\right]\psi(\mathbf{r}) \tag{83}$$

The meaning of Eq. (83) is this. If we know the value of a function at a 'point' $\mathbf{r}_1, \mathbf{r}_2, \ldots$, then we can calculate it at any other 'point' $\mathbf{r}_1', \mathbf{r}_2', \ldots$ which can be generated by a rotation provided we know the orbital angular momentum of the system about the axis of rotation. We shall see, later, that there are classes of wavefunctions for which it is not enough to know the orbital angular momentum to determine the state of the system for a rotated configuration. Writing

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*We shall sometimes write $\psi(\mathbf{r})$ for $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n)$.

$$R_n(\varphi) = \exp\left(\frac{i}{\hbar}\varphi\,\hat{\mathbf{n}}\cdot\mathbf{L}\right) \tag{84}$$

we have*

$$\psi(\mathbf{r}') = R_n(\varphi)\,\psi(\mathbf{r}) \tag{85}$$

The inverse operation is obtained by substituting $-\varphi$ for φ so that

$$R^{-1}(\varphi) = R(-\varphi) \tag{86}$$

We could go through the same arguments from the passive point of view. Here, we consider two co-ordinate systems Σ and Σ', the second obtained from the first by rotation about an axis $\hat{\mathbf{n}}$, by an angle $-\varphi$. Let $\mathbf{r}$ be the co-ordinate in Σ and $\mathbf{r}'$ the co-ordinate in Σ' of the same physical point. If the Σ observer defines the state of the system by $\psi(\mathbf{r})$, the Σ' observer will define the state by a different function $\psi'(\mathbf{r}')$. However, both measure the same amplitudes at a particular physical point. Hence

$$\psi(\mathbf{r}) = \psi'(\mathbf{r}') \tag{87}$$

For infinitesimal transformation

$$\mathbf{r}' = \mathbf{r} + \delta\varphi(\hat{\mathbf{n}}\times\mathbf{r}) \tag{88}$$

(It may be recalled that our axes are rotated by $-\delta\varphi$). Using the same logic as before, we see that

$$\psi'(\mathbf{r}') = \left(1 + \frac{i}{\hbar}\delta\varphi\,\hat{\mathbf{n}}\cdot\mathbf{L}\right)\psi'(\mathbf{r}) \tag{89}$$

and for a finite rotation

$$\psi'(\mathbf{r}') = \exp\left(\frac{i}{\hbar}\varphi\,\hat{\mathbf{n}}\cdot\mathbf{L}\right)\psi'(\mathbf{r}) \tag{90}$$

From Eqs. (87) and (90) we have

$$\psi'(\mathbf{r}) = \mathrm{epx}\left(-\frac{i}{\hbar}\varphi\,\hat{\mathbf{n}}\cdot\mathbf{L}\right)\psi(\mathbf{r}) \tag{91}$$

or,

$$\psi'(\mathbf{r}) = R_n^{-1}(\varphi)\,\psi(\mathbf{r}) \tag{92}$$

In the ensuing discussion we shall adopt the passive point of view.

6.8 Rotational Symmetry and Conservation of Angular Momentum

Let us first see how an operator transforms under the rotation discussed above. The problem posed is this: Suppose an observer in Σ constructs an operator** H

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*It must always be remembered that the co-ordinates $\mathbf{r}$ and $\mathbf{r}'$ are related through $\mathbf{r}' = \mathbf{r} + \varphi\,\hat{\mathbf{n}}\times\mathbf{r}$.

**We specialize our discussion to the Hamiltonian.

according to the recipe

$$H = H(\mathbf{r}) \tag{93}$$

i.e., given any set of co-ordinates the operator is known for that set. If now the observer in Σ' constructs his operator according to the rule $H'(\mathbf{r})$, what is the relationship between $H(\mathbf{r})$ and $H'(\mathbf{r})$? The two observers write their eigenvalue equations as

$$H(\mathbf{r})\,\psi(\mathbf{r}) = E\,\psi(\mathbf{r}) \tag{94}$$

$$H'(\mathbf{r})\,\psi'(\mathbf{r}) = E\,\psi'(\mathbf{r}) \tag{95}$$

Using Eqs. (92) and (95) we have

$$H'(\mathbf{r})\,R^{-1}\,\psi(\mathbf{r}) = E\,R^{-1}\,\psi(\mathbf{r}) \tag{96}$$

Multiplying by R on the left, we have

$$RH'(\mathbf{r})\,R^{-1}\,\psi(\mathbf{r}) = E\,\psi(\mathbf{r}) \tag{97}$$

Comparing this with Eq. (94), we see that H and H' are related through the *similarity* transformation

$$H(\mathbf{r}) = RH'(\mathbf{r})\,R^{-1} \tag{98}$$

In all known physical problems the Hamiltonian has the property that for two observers whose axes are rotated with respect to each other, the Hamiltonian is the same for the same argument $\mathbf{r}$, i.e., the function is the same. Thus

$$H'(\mathbf{r}) = H(\mathbf{r}) \tag{99}$$

Equation (99) is a physical statement that has to be verified by experiment. One knows of no result that is in contradiction with this. Equations (98) and (99) yield

$$[R, H] = 0 \tag{100}$$

If R refers to an arbitrary infinitesimal rotation it is easy to appreciate [see Eq. (82)] that this implies that

$$[\mathbf{L}, H] = 0 \tag{101}$$

This is precisely the condition that a system can have well defined eigenvalues of H and any one of the components of $\mathbf{L}$, since L_x, L_y, L_z do not commute among themselves, only one of them and L^2 can have well defined eigenvalues along with H. For an isolated system the energy and the eigenvalues of L^2 (and one of the components) will be constants of motion. Equation (100) is quite general. However, there are cases (e.g., when the wave function represents particles with spin angular momentum as well) where R is not simply related to the orbital angular momentum as in Eq. (84). In such cases Eq. (101) will not follow.

6.9 Degeneracy

Consider a function ψ which is a simultaneous eigenfunction of H and L_z. Since H also commutes with L_x and L_y, we have

$$H(L_x\psi) = L_x(H\psi) = L_x(E\psi) = E(L_x\psi) \tag{102}$$

Thus $L_x\psi$ is an eigenfunction of H with the same energy E. Moreover, since L_z and L_x do not commute, L_x cannot be well defined in the state* ψ, i.e.,

$$L_x\psi \neq \lambda\psi$$

Consequently, $\psi' = L_x\psi$ must represent a different state. Thus, whenever the Hamiltonian of a system commutes with a set of operators which do not commute among themselves, we expect degeneracies. (Another example of this is the permutation degeneracy for a system of identical particles**).

6.10 Reflection Invariance and Parity

We have introduced parity in Sec. 3.5. Here we discuss the general relationship between reflection invariance of the Hamiltonian and parity. We introduce the reflection operator by the relation

$$P\psi(\mathbf{r}) = \psi(-\mathbf{r}) \tag{103}$$

Since

$$P^2\psi(\mathbf{r}) = \psi(\mathbf{r})$$

the eigenvalues of P are obviously ± 1. Under the transformation P, the Hamiltonian will change into [exactly following the discussion leading to Eq. (98)]

$$H(-\mathbf{r}) = H'(\mathbf{r}) = PH(\mathbf{r})\,P^{-1}$$

Here one should interpret $H(\mathbf{r})$ as the Hamiltonian as written down by an observer in one frame of reference and $H'(\mathbf{r})$ as written down by the observer in the reflected frame. In most physical problems

$$H(-\mathbf{r}) = H'(\mathbf{r}) = H(\mathbf{r}) \tag{104}$$

Where the invariance [i.e., Eq. (104)] holds, we have

$$[P, H] = 0$$

so that eigenfunctions of H belong to a well defined eigenvalue of P, i.e., eigenfunctions of H have even or odd parity.

Angular momentum eigenfunctions clearly exhibit this property, In polar coordinates the effect of reflection is to change θ to $\pi - \theta$ and φ to $\pi + \varphi$. Now it can be shown that

$$Y_{lm}(\pi - \theta, \varphi + \pi) = (-1)^l\, Y_{lm}(\theta, \varphi)$$

Clearly eigenfunctions with even l have even parity and those with odd l have odd parity.

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*This is not true for an S (i.e., $l = 0$) state. Thus the conclusion about degeneracy is not valid for this state.

**See Landau and Lifshitz (1968).

The concept of parity is useful in deducing simple selection rules. In quantum mechanics the transition rates depend on matrix elements of some operator between the initial and final states. As an example, consider the so-called dipole transition (see Chapter 21) between the $2S$ and $1S$ states of the hydrogen atom. The relevant matrix element will be

$$\mathbf{M} = \langle 200 \,|\, \mathbf{p} \,|\, 100 \rangle$$

where the symbol 100 refers to the values of n, l and m and $\mathbf{p}$ is the dipole operator. Since $\mathbf{p} = e\mathbf{r}$ is an odd operator, it is easy to show that the matrix element vanishes. We have

$$\mathbf{M} = \iiint_{-\infty}^{\infty} \psi_{200}(\mathbf{r})\, \mathbf{p}\, \psi_{100}(\mathbf{r})\, d^3r$$

Changing the variable $\mathbf{r}$ to $-\mathbf{r}$ and using the results

$$\psi_{200}(-\mathbf{r}) = \psi_{200}(\mathbf{r}),\ \psi_{100}(-\mathbf{r}) = \psi_{100}(\mathbf{r}) \quad \text{and} \quad \mathbf{p}(-\mathbf{r}) = -\mathbf{p}(\mathbf{r})$$

we get

$$\mathbf{M} = -\iiint_{\infty}^{-\infty} \psi_{200}(-\mathbf{r})\, \mathbf{p}(-\mathbf{r})\, \psi_{100}(-\mathbf{r})\, d^3r$$

$$= -\iiint_{-\infty}^{\infty} \psi_{200}(\mathbf{r})\, \mathbf{p}(\mathbf{r})\, \psi_{100}(\mathbf{r})\, d^3r$$

or $\mathbf{M} = 0$. Thus $2S \rightarrow 1S$ dipole transition is forbidden. This, of course, is a special case of a general rule that odd operators do not connect states of the same parity—a jargon that simply means that the matrix element is zero.

PROBLEMS

Problem 6.1

Derive the commutation relations

(a)
$$\begin{aligned} [L_z, x] &= i\hbar y, & [L_z, p_x] &= i\hbar p_y \\ [L_z, y] &= -i\hbar x, & [L_z, p_y] &= -i\hbar p_x \\ [L_z, z] &= 0, & [L_z, p_z] &= 0 \text{ etc.} \end{aligned}$$

(b)
$$[L_x, r^2] = [L_y, r^2] = [L_z, r^2] = 0$$

Problem 6.2

Show that

$$\mathbf{L} \cdot \mathbf{p} = 0$$

and

$$\mathbf{L} \cdot \mathbf{r} = 0$$

PROBLEM 6.3

Assuming $R_z(\alpha) = 1 - (i/\hbar)\,\alpha\, L_z$ [see Eq. (68)] and similar relations for R_x and R_y, obtain explicit differential operator representations of L_x, L_y and L_z in spherical polar co-ordinates.

PROBLEM 6.4

Prove that

$$L^2 = L_x^2 + L_y^2 + L_z^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

PROBLEM 6.5

(a) We define the ladder operators

$$L_+ = L_x + iL_y \tag{105}$$

and

$$L_- = L_x - iL_y \tag{106}$$

Prove that

$$L^2 = \tfrac{1}{2}\,(L_+L_- + L_-L_+) + L_z^2 \tag{107}$$

(b) Substitute the differential operator representations of L_+ and L_- to prove Eq. (22).

PROBLEM 6.6

Using vector method, prove that

$$L^2\,\psi = (-i\hbar\,\mathbf{r}\times\nabla)^2\,\psi = -\hbar^2r^2\nabla^2\psi + \hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) \tag{108}$$

PROBLEM 6.7

Using the following representation of p_r

$$p_r = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \tag{109}$$

(see also Problem 8.16), prove that

$$\frac{p^2}{2m}\left(= -\frac{\hbar^2}{2m}\,\nabla^2\right) = \frac{p_r^2}{2m} + \frac{1}{2m}\,\frac{L^2}{r^2} \tag{110}$$

Interpret the above equation physically.

SOLUTIONS

SOLUTION 6.3

Let us suppose that when there is a rotation about the x-axis by an angle $\Delta\alpha$, θ becomes $\theta + \delta\theta$ and φ becomes $\varphi + \delta\varphi$; obviously, r remains unchanged. Now, for rotation about the z-axis [see Eq. (67)]

$$x \rightarrow x + y\,\Delta\alpha, \qquad y \rightarrow y - x\,\Delta\alpha, \qquad \text{and} \qquad z \rightarrow z$$

Similarly, for rotation about x-axis

$$y \to y + z\Delta\alpha, \qquad z \to z - y\Delta\alpha \quad \text{and} \quad x \to x$$

which are obtained by replacing z, x, y by x, y and z respectively. Thus

$$\delta x = \delta(r \sin\theta \cos\varphi) = 0$$

$$\delta y = \delta(r \sin\theta \sin\varphi) = z\Delta\alpha$$

and

$$\delta z = \delta(r \cos\theta) = -y\Delta\alpha$$

or

$$\cos\theta\,(\delta\theta)\cos\varphi - \sin\theta\sin\varphi\,\delta\varphi = 0$$

$$\cos\theta\,(\delta\theta)\sin\varphi + \sin\theta\cos\varphi\,\delta\varphi = \cos\theta\,\Delta\alpha$$

$$-\sin\theta\,\delta\theta = -\sin\theta\sin\varphi\,\Delta\alpha$$

which give

$$\delta\theta = \sin\varphi\,\Delta\alpha \tag{111}$$

and

$$\delta\varphi = \cot\theta\cot\varphi\,\delta\theta = \cot\theta\cos\varphi\,\Delta\alpha \tag{112}$$

Thus

$$R_x(\Delta\alpha)\,\psi(r, \theta, \varphi) = \psi(r, \theta + \delta\theta, \varphi + \delta\varphi)$$

$$= \psi(r, \theta, \varphi) + \frac{\partial\psi}{\partial\theta}\sin\varphi\,(\Delta\alpha) + \frac{\partial\psi}{\partial\varphi}\cot\theta\cos\varphi\,\Delta\alpha$$

But

$$R_x(\Delta\alpha)\,\psi(r, \theta, \varphi) = \left[1 + \frac{\Delta\alpha}{i\hbar}L_x\right]\psi$$

$$\therefore \qquad L_x = i\hbar\left[\sin\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\,\frac{\partial}{\partial\varphi}\right] \tag{113}$$

Similarly

$$L_y = i\hbar\left[-\cos\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\,\frac{\partial}{\partial\varphi}\right] \tag{114}$$

SOLUTION 6.5

(b) Using Eqs. (18) and (19), one readily obtains

$$L_+ = L_x + iL_y = i\hbar\, e^{i\varphi}\left(-i\,\frac{\partial}{\partial\theta} + \cot\theta\,\frac{\partial}{\partial\varphi}\right)$$

$$L_- = L_x - iL_y = i\hbar\, e^{-i\varphi}\left(i\,\frac{\partial}{\partial\theta} + \cot\theta\,\frac{\partial}{\partial\varphi}\right)$$

Thus

$$\begin{aligned}L_+L_-\psi &= (i\hbar)^2 e^{i\varphi}\Big[e^{-i\varphi}\frac{\partial^2\psi}{\partial\theta^2} - ie^{-i\varphi}\frac{\partial}{\partial\theta}\left(\cot\theta\frac{\partial\psi}{\partial\varphi}\right)\\ &\qquad -i\cot\theta\frac{\partial}{\partial\varphi}\left(e^{-i\varphi}\frac{\partial\psi}{\partial\theta}\right) + \cot^2\theta\frac{\partial}{\partial\varphi}\left(e^{-i\varphi}\frac{\partial\psi}{\partial\varphi}\right)\Big]\\ &= -\hbar^2\Big[\frac{\partial^2}{\partial\theta^2} + \frac{i}{\sin^2\theta}\frac{\partial}{\partial\varphi} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2}\\ &\qquad - i\cot^2\theta\frac{\partial^2}{\partial\varphi^2}\Big]\psi\end{aligned}$$

Therefore

$$L_+L_- = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2} + i\frac{\partial}{\partial\varphi}\right] \tag{115}$$

Similarly

$$L_-L_+ = -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2} - i\frac{\partial}{\partial\varphi}\right] \tag{116}$$

Since

$$L_z^2 = -\hbar^2\frac{\partial^2}{\partial\varphi^2}$$

we obtain

$$\begin{aligned}L^2 &= \tfrac{1}{2}(L_+L_- + L_-L_+) + L_z^2\\ &= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\varphi}\frac{\partial^2}{\partial\varphi^2}\right]\end{aligned}$$

SOLUTION 6.6

$$\begin{aligned}L^2\psi &= (-i\hbar\,\mathbf{r}\times\nabla)^2\psi = -\hbar^2\mathbf{r}\times\nabla\cdot(\mathbf{r}\times\nabla\psi)\\ &= -\hbar^2\mathbf{r}\cdot[\nabla\times(\mathbf{r}\times\nabla\psi)] \text{ (by interchanging the dot and cross)}\\ &= \hbar^2\mathbf{r}\cdot[(\nabla\psi\cdot\nabla)\mathbf{r} - (\mathbf{r}\cdot\nabla)\nabla\psi - \nabla\psi(\nabla\cdot\mathbf{r}) + \mathbf{r}(\nabla\cdot\nabla\psi)]\end{aligned}$$

where we have used a vector identity. Thus

$$\begin{aligned}L^2\psi &= -\hbar^2\left[r\frac{\partial\psi}{\partial r} - \mathbf{r}\cdot\left(r\frac{\partial}{\partial r}\nabla\psi\right) - r\frac{\partial\psi}{\partial r}3 + r^2\nabla^2\psi\right]\\ &= -\hbar^2\left[-2r\frac{\partial\psi}{\partial r} - r^2\frac{\partial^2\psi}{\partial r^2} + r^2\nabla^2\psi\right]\\ &= -\hbar^2r^2\left[\nabla^2\psi - \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\right]\\ &= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]\end{aligned}$$

SOLUTION 6.7

$$\frac{p_r^2}{2m}\psi = -\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)\psi$$

$$= -\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial r^2} - \frac{\psi}{r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\psi\right]$$

$$= -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\right]$$

Using this Eq. (110) follows immediately. Now, in classical mechanics, the kinetic energy of a particle (in spherical polar co-ordinates) is $p_r^2/2m + L^2/2mr^2$ where p_r represents the radial component of the momentum and L^2 the square of the angular momemtum*. Thus, in quantum mechanics the radial component of the angular momentum is represented by Eq. (109).

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*Classically,

$$\mathbf{L} = (\mathbf{r} \times \mathbf{p}) = rp_\theta\hat{\theta} - rp_\varphi\hat{\varphi}$$

Therefore $L^2 = r^2p_\theta^2 + r^2p_\varphi^2$ and

$$p^2 = p_r^2 + p_\theta^2 + p_\varphi^2 = p_r^2 + \frac{L^2}{r^2}.$$

CHAPTER SEVEN

Vector Spaces

7.1 Function Space

In quantum mechanics we use words like orthogonal functions, linearly independent Hilbert space, etc., which conjure up a picture of vectors in a strange space and we are not clear about what really those entities are. The difficulty is that, while abstraction is desirable and even essential in later stages, insistence on rigour and abstraction deters the student from understanding very simple ideas. In this chapter we will try to develop an understanding of what we imply by words like 'orthogonal functions' and also introduce vector spaces; these concepts will be useful in understanding the next chapter.

Suppose we want to describe the behaviour of a function—say $f(x) = x^2$ in a definite interval $x = -1$ to $+1$. A complete knowledge of this function means that we know $f(x)$ for an infinite number (non-denumerable) of values of x. Suppose, however, we limit our ambition and want to represent $f(x)$ for $x = -1, 0$ and $+1$. We call these values of x as x_1, x_2 and x_3. We erect 3 axes (cartesian) and represent the value that $f(x_1)$ takes along axis 1, $f(x_2)$ along axis 2, etc. Note that it is the value $f(x_1)$ which is measured off along axis 1, etc. Then, for representing $f(x)$ for only these 3 values, a single vector joining the origin to the point 1, 0, 1 will do the trick. Similarly, the function $f(x) = x$ will, on the same diagram be the vector joining the origin to the point -1, 0, 1, etc. It may be noted that the vector representing $f(x) = 4x^2$ is in the same direction as the vector representing $f(x) = x^2$. For the sake of convenience, we can normalize all such vectors to be of unit length and in this particular case the function $f(x) = x^2/\sqrt{2}$ is normalized. Similarly, the function $x/\sqrt{2}$ is also a normalized function.

Moreover, we can imagine erecting 3 vectors mutually perpendicular representing 3 *basis functions*. Any *function* (as long as our interest is only in 3 values of x, i.e., x_1, x_2 and x_3) can be represented as a linear combination of the 3 basis functions. Let us try three such functions

$$f(x) = \frac{x}{\sqrt{2}}, \quad g(x) = \frac{x^2}{\sqrt{2}}, \quad h(x) = 1 - x^2 \tag{1}$$

They form an orthonormal set in the sense that the representing vectors

$$\left[-\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]; \quad \left[\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right]; (0, 1, 0) \tag{2}$$

are mutually perpendicular and each vector is of unit length (i.e., they are normalized). We now assert that any *function* requiring only the specification at $x = -1, 0$ and 1 is a linear combination of f, g and h. For example, the function

$u(x) = 3 + x$ gives the vector (2, 3, 4) and is given by the following linear combination

$$u(x) = \sqrt{2} f(x) + 3\sqrt{2} g(x) + 3h(x) \tag{3}$$

(The coefficients are easily obtained by evaluating the scalar product of the orthonormal vectors f, g and h with u.)

We can generalize this to n dimensions, i.e., if we want to represent functions at n points $x_1, x_2, \ldots, x_n$ we can do so in an n-dimensional diagram. The vector for $f(x)$ will be the line joining the origin to the point $f(x_1), f(x_2), \ldots, f(x_n)$ where we lay off measures $f(x_1)$ along 1-axis, $f(x_2)$ along 2-axis, etc. Once again, it should be remembered that it is the values of $f(x)$ that are plotted along the n-axes and the function is represented by a single vector. We can normalize the vector by demanding

$$\sum_{j=1}^{n} [f(x_j)]^2 = 1 \tag{4}$$

Thus if $f(x) \sim x^2$, we simply try $f(x) = ax^2$ and adjust a. Next, we need n linearly independent such functions

$$f_1(x), f_2(x), \ldots f_n(x)$$

By linearly independent we imply that none of the functions should be expressible as a linear combination of the remaining $(n - 1)$ functions. This means we have

$$\sum_{p=1}^{n} a_p f_p(x_j) \neq 0 \tag{5}$$

for any set of numbers a_1 to a_n for all x_j $(j = 1, \ldots, n)$.

We can generalize these ideas to include a continuous range of values of x in the interval $a \leqslant x \leqslant b$ by letting n go to infinity. But now we come across a problem. How do we know that for a function $f(x)$

$$\operatorname*{Lt}_{n\to\infty} \sum_{j=1}^{n} [f(x_j)]^2 \tag{6}$$

is finite? In fact, it will be generally infinite—since each $f(x_j)$ is finite. We adopt a stratagem. We assume $x_1, x_2, \ldots$ to be equally spaced and instead of plotting $f(x_j)$ along the j-axis we plot $f(x_j)\sqrt{h}$, where

$$h = \frac{b-a}{n} = dx \tag{7}$$

Then normalization requires

$$\int_a^b [f(x)]^2\, dx \quad \text{should be finite.} \tag{8}$$

This is a reasonable condition for most functions.

We next consider n vectors $f_1(x), f_2(x), \ldots, f_n(x)$; these will be orthogonal if

$$\sum_{j=1}^{n} f_\rho(x_j)\, f_\mu(x_j) = 0 \qquad \rho \neq \mu \tag{9}$$

For $n \to \infty$ and with $x_1, x_2, \ldots$ equally spaced, Eq. (9) works out as

$$\int_a^b f_\rho(x)\, f_\mu(x)\, dx = 0 \qquad \rho \neq \mu \tag{10}$$

We then call f_ρ and f_μ orthogonal and we now have a vivid picture of why we call them so.

Unfortunately, in quantum mechanics, we deal with complex functions and we need to modify our ideas slightly. We do this by demanding

$$\int_a^b |f_\rho(x)|^2\, dx = 1 \qquad \text{for all } \rho \tag{11}$$

and
$$\int_a^b f_\rho^*(x)\, f_\mu(x)\, dx = 0 \qquad \text{for } \rho \neq \mu \tag{12}$$

Equations (11) and (12) constitute the orthonormality condition [cf. Eqs. (20) and (21) of Chapter 3].

An example of an orthonormal set of functions are the trigonometric functions $\sin nx$ and $\cos nx$ in the interval $0 \leqslant x \leqslant 2\pi$.

$$\left.\begin{aligned} &\int_0^{2\pi} \sin nx \cos mx\, dx = 0 \qquad \text{all } n, m \\ &\int_0^{2\pi} \sin nx \sin mx\, dx = \pi\delta_{nm}, \quad \text{etc.} \end{aligned}\right\} \tag{13}$$

We can, of course, normalize these easily. Such a space of functions is called a function space $\mathcal{L}$. In such a function space, each normalized function $\phi_p(x)$ ($p = 0, 1, 2, \ldots$) is a vector. If the functions $\phi_p(x)$ form a complete set in this space then any function $f(x)$ can be expressed as a linear combination of $\phi_p(x)$. Indeed $f(x)$ itself is a vector in this space.

7.2 Operators

Frequently, we have to study operations which change a function $f(x)$ to another function $g(x)$. For example $f(x)$ may be $\sin^2 x$ and the operation may be $T = d/dx$. Then

$$g(x) = 2 \sin x \cos x = \sin 2x$$

Note that $f(x) = \frac{1}{2}(\cos 2x - 1)$ is a vector with components along the function axes cos mx, $m = 2, 0$; i.e., $f(x)$ is a vector in a *plane* of the $m = 2, 0$ basis vectors cos mx. Then the operator T rotates $f(x)$ to a vector $g(x)$ which, in this case is entirely along the sin $2x$ axis.

Since every function (vector) can be expanded in terms of the basis functions of the space $\mathcal{L}$, we can predict the effect of T on any $f(x)$ provided we know the effect of T on each basis function $\phi_\rho(x)$. Moreover, this effect is merely to rotate $\phi_\rho(x)$ to another vector which is a linear combination of the basis functions

$$\phi'_\rho(x) = T\phi_\rho(x) = \sum_\mu T_{\mu\rho}\,\varphi_\mu(x) \tag{14}$$

Thus the entire operator T is specified by knowing the complete matrix T_{11}, $T_{12}, \ldots T_{21}, T_{22}, \ldots$. We then call the matrix T the representation of the operator T. Obviously, using the orthonormality condition we immediately obtain

$$T_{\mu\rho} = \int \phi^*_\mu(x)\;\phi'_\rho(x)\,dx = \int \phi^*_\mu(x)\,T\phi_\rho(x)\,dx \tag{15}$$

Now, in matrix form, if we write

$$\Phi = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \vdots \end{pmatrix} \tag{16}$$

then $\quad \Phi' = T\Phi \qquad (17)$

The above definition of operator is still far too general for our purpose. In quantum mechanics, we essentially deal with operators which leave products such as $|\int f^*(x)\,g(x)\,dx\,|^2$ invariant under transformations. This requires us to study a special kind of operator, namely, the linear operator. For an operator to be linear, we must have

$$T(C_1 f + C_2 g) = C_1 Tf + C_2 Tg \tag{18}$$

where C_1 and C_2 are constants. We can now define Hermitian operators

$$\int g^*\,Tf\,dx = \int (Tg)^*\;dx f \tag{19}$$

which will give

$$T_{\mu\nu} = T^*_{\nu\mu} \tag{20}$$

Often we deal with operators which do not change the 'length' of the vectors; i.e.,

$$1 = \int \phi'^*_\rho(x)\,\phi'_\rho(x)\,dx = \sum_\lambda\sum_\mu \int T^*_{\mu\rho}\,\phi^*_\mu\,T_{\lambda\rho}\,\phi_\lambda\,dx$$

$$= \sum_\lambda\sum_\mu T^*_{\mu\rho}\,T_{\lambda\rho}\,\delta_{\mu\lambda} = \sum_\lambda T^*_{\lambda\rho}\,T_{\lambda\rho} \tag{21}$$

Thus

$$TT^{\dagger} = 1 = TT^{\dagger} \tag{22}$$

where

$$(T^{\dagger})_{\rho\lambda} = T^{*}_{\lambda\rho} \tag{23}$$

Operators satisfying Eq. (21) are known as unitary operators (see also Sec. 8.11). It is seen that Hermitian operators are represented by Hermitian matrices and unitary operators by unitary matrices.

7.3 An Example : Coupled Pendulums

As a simple example of the use of vector spaces, we consider the oscillations of a pair of coupled pendulums of equal length l (see Fig. 7.1). We write

$$\ddot{x}_1 = -\left(\frac{g}{l} + \frac{k}{M}\right)x_1 + \frac{k}{M}x_2 \tag{24}$$

$$\ddot{x}_2 = -\left(\frac{g}{l} + \frac{k}{M}\right)x_2 + \frac{k}{M}x_1 \tag{25}$$

where x_1 and x_2 are (small) displacements from the mean positions, k the spring constant, M the mass and g the acceleration due to gravity. To decouple the variables x_1 and x_2, we form linear combinations

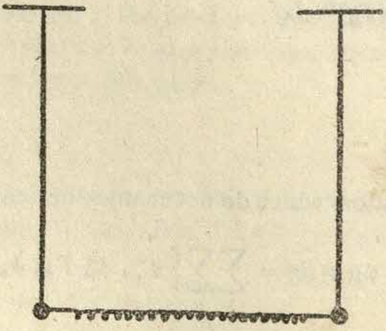
$$\begin{aligned} x_s &= (x_1 + x_2)/\sqrt{2} \\ x_a &= (x_1 - x_2)/\sqrt{2} \end{aligned} \tag{26}$$

to obtain

$$\ddot{x}_s = -\omega_0^2\, x_s$$

and $$\ddot{x}_a = -\omega_1^2\, x_a \tag{27}$$

where $\omega_0^2 = g/l$



and $$\omega_1^2 = \frac{g}{l} - \frac{2k}{M} \tag{28}$$

so that

$$\begin{aligned} x_s(t) &= A_s \sin(\omega_0 t + \phi_s) \\ x_a(t) &= A_a \sin(\omega_1 t + \phi_a) \end{aligned} \tag{29}$$

x_s and x_a are the normal co-ordinates of the system. From Eq. (26) we can solve for x_1 and x_2 to obtain

$$\begin{aligned} x_1(t) &= (x_s + x_a)/\sqrt{2} \\ x_2(t) &= (x_s - x_a)/\sqrt{2} \end{aligned} \tag{30}$$

Now how do we represent such a system in a vector space? Assume, first, that we are interested in the values of x_1 and x_2 at a particular time t. We construct a two-dimensional vector space with the values $x_1(t)$ and $x_2(t)$ laid off along the x and y axes. Thus a vector

$$\mathbf{r}(t) = \hat{\mathbf{e}}_x x_1(t) + \hat{\mathbf{e}}_y x_2(t)$$

will represent our system, $\hat{e}_x$ and $\hat{e}_y$ being the unit vectors along x and y axes. (Note that we are not representing x_1 and x_2 for different values of t in this plot.)

In this two dimensional space, the vector $\mathbf{r}$ will change with time. From Eqs. (24) and (25) we may write

$$\begin{aligned} \frac{d^2\mathbf{r}(t)}{dt^2} &= \left[-\left(\frac{g}{l} + \frac{k}{M}\right)x_1 + \frac{k}{M}x_2\right]\hat{e}_x + \left[\frac{k}{M}x_1 - \left(\frac{g}{l} + \frac{k}{M}\right)x_2\right]\hat{e}_y \\ &= \mathrm{S}(t) \end{aligned} \tag{31}$$

The vector $\mathrm{S}(t)$ will in general be different from $\mathbf{r}$ so that we may regard the effect of the operator d^2/dt^2 as one of rotating (and, in this case, also changing the length of) the vectorr (t).

Instead of x_1 and x_2 we may wish to represent x_s and x_a. We rotate the x and y axes by 45° and the new components are

$$x_s = \frac{x_1 + x_2}{\sqrt{2}} \quad \text{and} \quad x_a = \frac{x_1 - x_2}{\sqrt{2}}$$

In this frame Eqs. (27) tell us that vectors directed along x_s (or x_a) are *not* rotated by the operator d^2/dt^2. This, then, is the distinctive property of normal co-ordinates.

Now the vector $\mathbf{r}$ can also be represented by a column matrix

$$\mathbf{r} = \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \tag{32}$$

so that Eq. (31) can be written as

$$\frac{d^2\mathbf{r}}{dt^2} = \hat{A}\mathbf{r} \tag{33}$$

where $\hat{A}$ is the 2 × 2 matrix

$$\begin{bmatrix} -\left(\frac{g}{l} + \frac{k}{M}\right) & \frac{k}{M} \\ \frac{k}{M} & -\left(\frac{g}{l} + \frac{k}{M}\right) \end{bmatrix} \tag{34}$$

We are therefore searching for a new *basis* for the vector $\mathbf{r}$ in which Eq. (33) would reduce to

$$\frac{d^2\mathbf{x}}{dt^2} = \hat{A}\mathbf{x} = a\mathbf{x} \tag{35}$$

where a is a number. This is an eigenvalue problem; i.e., we have to find the eigen-values of the matrix A. This is done by setting the determinant

$$\begin{vmatrix} a_{11} - \lambda & a_{12} \\ a_{21} & a_{22} - \lambda \end{vmatrix} = 0$$

where $a_{11}, a_{12}, a_{21}, a_{22}$ are the elements of the matrix A. The two solutions of λ are then the eigenvalues we seek and the corresponding eigenvectors are x_s and x_a.

The relevance of this discussion to quantum mechanics is, as we shall see in Chapter 8, that the state of a quantum system is described by a vector in an abstract space, often infinite dimensional. An *observable* is represented by an operator and its eigenvalues are the spectrum of values that one obtains on a measurement of the physical quantity corresponding to the observable.

7.4. Bra and Ket Vectors

It is convenient to represent a column vector

$$\begin{bmatrix} x_1 \\ x_2 \\ \vdots \end{bmatrix} \text{ by the symbol } | x \rangle$$

called the ket x. A scalar product is obtained by taking the matrix product

$$[x_1, x_2 \ldots] \begin{bmatrix} x_1 \\ x_2 \\ \vdots \end{bmatrix} = x_1^2 + x_2^2 + \ldots$$

However, in quantum mechanics, the numbers $x_1, x_2, \ldots$ are, in general, complex, so that it is appropriate to define the scalar product as

$$[x_1^*, x_2^*, \ldots] \begin{bmatrix} x_1 \\ x_2 \\ \vdots \end{bmatrix} = |x_1|^2 + |x_2|^2 + \ldots$$

Accordingly, we denote the row vector, corresponding to the column vector $|x\rangle$ by

$$\langle x| \rightarrow [x_1^*, x_2^*, \ldots]$$

$\langle x|$ is called the bra x. [The product $\langle x \mid x\rangle$ is a bra(c)ket!]. More generally, a scalar product is of the form $\langle x \mid y\rangle$ and it will be a complex number. Note that

$$\langle x \mid y\rangle = \langle y \mid x\rangle^*$$

In the next chapter, we deal with the algebra of bra and ket vectors.

CHAPTER EIGHT

The Bra and Ket Algebra

8.1 Introduction

In the earlier chapters, we had developed quantum mechanics by obtaining the Schrödinger equation and solving it for problems of physical interest. In this chapter we will develop what is known as the matrix formulation of quantum mechanics* in which the states of a dynamical system will be denoted by certain vectors (which will be called, following Dirac, as bra and ket vectors) and operators representing dynamical variables (like position co-ordinates, components of momentum and angular momentum, energy, etc.) by matrices.

In Sec. 8.2 we will discuss the vector representation of states. In Secs. 8.3-8.7 we will discuss linear operators and develop the algebra involving bra and ket vectors and linear operators. This algebra is due to Dirac and for a detailed and thorough treatment, the reader is referred to the classic treatise of Dirac (1958); an authoritative account can also be found in Messiah (1970). In Sec. 8.8 we will discuss the relationship between the bra and ket vectors and the wave functions introduced in Chapters 2-6. In Sec. 8.9 we will show how the bra and ket algebra can be used to solve the harmonic oscillator problem; the basic assumption will be the commutation relation. In a similar manner we will solve the angular momentum problem in the next chapter, once again the basic relation will be the commutation relation. In Sec. 8.10 we will show that if the operators corresponding to two observables commute, one can construct a complete set of simultaneous eigenkets. In Sec. 8.11 we will briefly consider the unitary transformation and in Secs. 8.12 and 8.13 we will develop the Schrödinger, Heisenberg and Interaction pictures; these will be used in later Chapters. Finally, in Sec. 8.14 we will introduce the density operator which plays a very important role in statistical mechanics.

8.2 Vector Representation of States : The Bra and Ket Vectors**

Because of the superposition principle (which allows one to superpose two states

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*It is worthwhile to point out that historically it was the matrix formulation which was introduced first by Heisenberg in his paper entitled 'The Interpretation of Kinematic and Mechanical Relationships according to the Quantum Theory' (*Zeitschrift fur Physik*, **33**, 879, 1925). This formulation was further developed by Born and Jordan in their paper entitled 'Quantum Mechanics' (*Zeitschrift fur Physik*, **34**, 858, 1925). Schrödinger's papers came later. His three famous papers were under the same title 'Quantization as an Eigenvalue Problem' and all the papers were published in *Annalen der Physik* (**79**, 361, 1926; **79**, 489, 1926; **81**, 109, 1926). In between, he had also published a paper with the self-explanatory title 'On the Relationship of the Heisenberg-Born-Jordan Quantum Mechanics to Mine' (*Annalen der Physik* **79**, 734, 1926). All the abovementioned papers by Heisenberg, Born, Jordan and Schrödinger are reproduced in a book by Ludwig (1968).

**Sections 8.2-8.5 are adapted from Dirac (1958); this is with the kind permission of Oxford University Press.

to get other states of the system) it is possible to represent every state of a dynamical system by a certain type of vector which, following Dirac (1958), we call as a *ket vector* or simply a *ket* and represent it by the symbol $| \rangle$. In order to distinguish different kets we insert a label; thus the state A of the dynamical system is represented by the symbol $| A \rangle$ and is read as 'ket A'.

The kets form a linear vector space*; i.e., any linear combination of ket vectors is also a ket vector in the same space. For example, if we have two ket vectors $| A \rangle$ and $| B \rangle$ then the linear combination

$$c_1 | A \rangle + c_2 | B \rangle$$

is also a ket vector in the same space; here c_1 and c_2 are arbitrary complex numbers. Thus, to quote Dirac, 'each state of a dynamical system at a particular time corresponds to a ket vector, the correspondence being such that if a state results from the superposition of certain other states, its corresponding ket vector is expressible linearly in terms of the corresponding ket vectors of the other states, and conversely.' Further, the kets $| A \rangle$ and $c | A \rangle$ (where c is an arbitrary non-zero complex number) correspond to the same state. In other words the state of the system is defined by the 'direction' of the vectors. In this respect the superposition principle in classical and quantum theories differ. For example, the superposition of a vibrating string on itself gives, in classical physics, a mode with twice the amplitude and four times the energy of the initial state of vibration. In contrast, in quantum mechanics, the superposition of a state on itself gives the same state.

Now, with every vector space there can be associated a dual vector space such that one can form a scalar product of the two vectors, one from each space. The vectors of the space dual to that of the ket vectors will be called bra vectors or simply '*bras*' and will be denoted by $\langle |$. The scalar product of the ket $| A \rangle$ and bra $\langle B |$ is denoted by $\langle B | A \rangle$ and is a complex number.

A bra is said to be a null bra if the scalar product vanishes for any ket, thus

$$\langle B | = 0 \quad \text{if} \quad \langle B | A \rangle = 0 \quad \text{for any } | A \rangle \tag{1}$$

Two bras are said to be equal if their scalar product with an arbitrary ket are equal, thus

$$\langle B_1 | = \langle B_2 | \quad \text{if} \quad \langle B_1 | A \rangle = \langle B_2 | A \rangle \quad \text{for any } | A \rangle \tag{2}$$

It is further assumed that

(i) There is a one to one correspondence between kets and bras in the sense that a state of a dynamical system represented by $| A \rangle$ can be equally well represented by the corresponding bra $\langle A |$. Further, if

$$| P \rangle = | A \rangle + | B \rangle \quad \text{then} \quad \langle P | = \langle A | + \langle B | \tag{3}$$

and if

$$| R \rangle = c | A \rangle \quad \text{then} \quad \langle R | = \overline{c} \langle A | \tag{4}$$

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*A rigorous treatment of finite dimensional vector spaces can be found in Halmos (1948).

CHAPTER EIGHT

The Bra and Ket Algebra

8.1 Introduction

In the earlier chapters, we had developed quantum mechanics by obtaining the Schrödinger equation and solving it for problems of physical interest. In this chapter we will develop what is known as the matrix formulation of quantum mechanics[*] in which the states of a dynamical system will be denoted by certain vectors (which will be called, following Dirac, as bra and ket vectors) and operators representing dynamical variables (like position co-ordinates, components of momentum and angular momentum, energy, etc.) by matrices.

In Sec. 8.2 we will discuss the vector representation of states. In Secs. 8.3-8.7 we will discuss linear operators and develop the algebra involving bra and ket vectors and linear operators. This algebra is due to Dirac and for a detailed and thorough treatment, the reader is referred to the classic treatise of Dirac (1958); an authoritative account can also be found in Messiah (1970). In Sec. 8.8 we will discuss the relationship between the bra and ket vectors and the wave functions introduced in Chapters 2-6. In Sec. 8.9 we will show how the bra and ket algebra can be used to solve the harmonic oscillator problem; the basic assumption will be the commutation relation. In a similar manner we will solve the angular momentum problem in the next chapter, once again the basic relation will be the commutation relation. In Sec. 8.10 we will show that if the operators corresponding to two observables commute, one can construct a complete set of simultaneous eigenkets. In Sec. 8.11 we will briefly consider the unitary transformation and in Secs. 8.12 and 8.13 we will develop the Schrödinger, Heisenberg and Interaction pictures; these will be used in later Chapters. Finally, in Sec. 8.14 we will introduce the density operator which plays a very important role in statistical mechanics.

8.2 Vector Representation of States : The Bra and Ket Vectors[**]

Because of the superposition principle (which allows one to superpose two states to get other states of the system) it is possible to represent every state of a dynamical system by a certain type of vector which, following Dirac (1958), we call as a *ket vector* or simply a *ket* and represent it by the symbol $| \rangle$. In order to distinguish different kets we insert a label; thus the state A of the dynamical system is represented by the symbol $| A\rangle$ and is read as 'ket A'.

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A bra is said to be a null bra if the scalar product vanishes for any ket, thus

$$\langle B | = 0 \quad \text{if} \quad \langle B | A\rangle = 0 \quad \text{for any } | A\rangle \tag{1}$$

Two bras are said to be equal if their scalar product with an arbitrary ket are equal, thus

$$\langle B_1 | = \langle B_2 | \quad \text{if} \quad \langle B_1 | A\rangle = \langle B_2 | A\rangle \quad \text{for any } | A\rangle \tag{2}$$

It is further assumed that

(i) There is a one to one correspondence between kets and bras in the sense that a state of a dynamical system represented by $| A\rangle$ can be equally well represented by the corresponding bra $\langle A |$. Further, if

$$| P\rangle = | A\rangle + | B\rangle \qquad \text{then} \quad \langle P | = \langle A | + \langle B | \tag{3}$$

and if

$$| R\rangle = c \,| A\rangle \qquad \text{then} \quad \langle R | = \bar{c}\langle A | \tag{4}$$

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*A rigorous treatment of finite dimensional vector spaces can be found in Halmos (1948).

where c is a complex number and $\bar{c}$ its complex conjugate.

(ii) $$\langle A \mid B \rangle = \overline{\langle B \mid A \rangle} \tag{5}$$

where the bar on the top implies the complex conjugate of the quantity. Putting $\mid B \rangle = \mid A \rangle$ we get

$$\langle A \mid A \rangle = \overline{\langle A \mid A \rangle}$$

implying that the scalar product $\langle A \mid A \rangle$ is a real number. We further assert that

$$\langle A \mid A \rangle \geqslant 0 \tag{6}$$

the equality sign holds only when $\mid A \rangle = 0$, i.e., $\mid A \rangle$ is a null ket.

If $\langle A \mid B \rangle = 0$ then the kets $\mid A \rangle$ and $\mid B \rangle$ are said to be orthogonal to each other. If

$$\langle A \mid A \rangle = 1$$

then the ket $\mid A \rangle$ is said to be normalized. Since the kets $\mid A \rangle$ and $c \mid A \rangle$ correspond to the same state we may always associate normalized kets to each state. Even then, a normalized ket is defined only within an arbitrary phase factor $e^{i\gamma}$ (where γ is a real number).

8.3 Linear Operators

An operator α converts a ket $\mid A \rangle$ into another ket $\mid B \rangle$

$$\mid B \rangle = \alpha \mid A \rangle \tag{7}$$

The above equation reads as: the ket $\mid B \rangle$ equals the operator α applied to the ket $\mid A \rangle$. One may picture the action of an operator as that of *rotating* a ket vector to another ket (see Sec. 7.2). An operator is said to be linear if it satisfies the following equation

$$\alpha(c_1 \mid A_1 \rangle + c_2 \mid A_2 \rangle + \ldots) = c_1 \alpha \mid A_1 \rangle + c_2 \alpha \mid A_2 \rangle + \ldots \tag{8}$$

where $c_1, c_2, \ldots$ are arbitrary complex numbers. Henceforth, we will consider only linear operators. An operator α is said to be a *null* operator if

$$\alpha \mid A \rangle = 0 \qquad \text{for any} \mid A \rangle \tag{9}$$

Thus a necessary and sufficient condition for an operator to be a *null* operator is

$$\langle A \mid \alpha \mid A \rangle = 0 \qquad \text{for any} \mid A \rangle \tag{10}$$

An operator α is said to be an unit operator if

$$\alpha \mid A \rangle = \mid A \rangle \qquad \text{for any} \mid A \rangle \tag{11}$$

It can be easily seen that a number can be regarded as a linear operator. Two operators α and β are said to be equal if and only if

$$\langle A \mid \alpha \mid A \rangle = \langle A \mid \beta \mid A \rangle \qquad \text{for any} \quad \mid A \rangle \tag{12}$$

The sum (or difference) of two operators α and β is defined through the equation

$$(\alpha \pm \beta) \mid A \rangle = \alpha \mid A \rangle \pm \beta \mid A \rangle \tag{13}$$

Further

$$\alpha + (\beta + \gamma) = (\alpha + \beta) + \gamma = \alpha + \beta + \gamma \tag{14}$$

and

$$(c_1 \alpha) \mid A \rangle = c_1 (\alpha \mid A \rangle) \tag{15}$$

where c_1 is an arbitrary complex constant. The product of two operators α and β is defined through the equation

$$(\beta\alpha) \mid A \rangle = \beta(\alpha \mid A \rangle) = \beta \mid B \rangle \tag{16}$$

where $\mid B \rangle = \alpha \mid A \rangle$. In general

$$\beta\alpha \neq \alpha\beta.$$

The commutator of two operators is defined by (see Sec. 2.3)

$$[\alpha, \beta] = \alpha\beta - \beta\alpha = -[\beta, \alpha] \tag{17}$$

So for we have assumed a linear operator to act on kets; we can make a linear operator α to operate on bras as well, the rule is that the bra has to be put on the left of the operator like $\langle P \mid \alpha$ and the operation is defined through the equation

$$\begin{aligned} \{\langle P \mid \alpha\} \mid A \rangle &= \langle P \mid \{\alpha \mid A \rangle\} \qquad \text{for any} \quad \mid A \rangle \\ &= \langle P \mid B \rangle, \ \mid B \rangle = \alpha \mid A \rangle \end{aligned}$$

(The combination $\alpha \langle B \mid$ is meaningless). Indeed because of the associative law we need not put any brackets and write simply as

$$\langle P \mid \alpha\beta\gamma \mid A \rangle$$

It is interesting to note that the combination $\mid B \rangle \langle A \mid$ can be considered as a linear operator because

$$\begin{aligned} \{ \mid B \rangle \langle A \mid \} \mid P \rangle &= \mid B \rangle \{\langle A \mid P \rangle\} \\ &= c \mid B \rangle \end{aligned}$$

because $\langle A \mid P \rangle$ $(=c)$ is just a complex number.

The adjoint of the operator α is denoted by $\bar{\alpha}$ and is defined through the equation

$$\langle A \mid \bar{\alpha} \mid B \rangle = \overline{\langle B \mid \alpha \mid A \rangle} \tag{18}$$

where $\overline{\langle B \mid \alpha \mid A \rangle}$ is the complex conjugate of the number $\langle B \mid \alpha \mid A \rangle$. Now

$$\begin{aligned}\langle A \mid \bar{\bar{\alpha}} \mid B \rangle &= \langle A \mid \bar{\beta} \mid B \rangle \qquad (\bar{\beta} \equiv \alpha) \\ &= \overline{\langle B \mid \beta \mid A \rangle} = \overline{\langle B \mid \bar{\alpha} \mid A \rangle} \\ &= \overline{\overline{\langle B \mid \alpha \mid A \rangle}} = \langle B \mid \alpha \mid A \rangle \end{aligned} \tag{19}$$

because the complex conjugate of the complex conjugate of a number is the original number itself. Since Eq. (19) holds for arbitrary $\mid A \rangle$ and $\mid B \rangle$ we have

$$\bar{\bar{\alpha}} = \alpha \tag{20}$$

i.e., the adjoint of the adjoint of a linear operator is the original operator itself. Further, the adjoint of the product of the two operators α and β is the product of the adjoint of the two operators in reverse order, i.e.,

$$\overline{\alpha\beta} = \bar{\beta}\,\bar{\alpha} \tag{21}$$

The proof is straightforward. Let

$$\alpha \mid A \rangle = \mid P \rangle$$

then

$$\begin{aligned}\langle A \mid \bar{\alpha} \mid B \rangle &= \overline{\langle B \mid \alpha \mid A \rangle} = \overline{\langle B \mid P \rangle} \\ &= \langle P \mid B \rangle \text{ [using Eq. (5)]}\end{aligned}$$

Since the above equation holds for arbitrary $\mid B \rangle$ we have

$$\langle P \mid = \langle A \mid \bar{\alpha} = \text{conjugate of } \alpha \mid A \rangle \tag{22}$$

Thus, if

$$\mid Q \rangle = \alpha\beta \mid A \rangle$$

then

$$\langle Q \mid = \langle A \mid \overline{\alpha\beta} \tag{23}$$

But, if we write

$$\mid Q \rangle = \alpha\beta \mid A \rangle = \alpha \mid R \rangle$$

where $\mid R \rangle = \beta \mid A \rangle$ (consequently $\langle R \mid = \langle A \mid \bar{\beta}$) then

$$\langle Q \mid = \langle R \mid \bar{\alpha} = \langle A \mid \bar{\beta}\,\bar{\alpha} \tag{24}$$

Comparing Eqs. (23) and (24) we get Eq. (21). In general

$$\overline{\alpha\beta\gamma\ldots} = \ldots\bar{\gamma}\,\bar{\beta}\,\bar{\alpha} \tag{25}$$

An operator is said to be self-adjoint if

$$\bar{\alpha} = \alpha \tag{26}$$

A self-adjoint operator is also called a real operator or a Hermitian operator.

8.4 The Eigenvalue Equation

For the linear operator α, consider the equation

$$\alpha \mid A_n \rangle = a_n \mid A_n \rangle \tag{27}$$

where a_n is an arbitrary complex number. Equation (27) represents an eigenvalue equation; the $\mid A_n \rangle$ s are known as the eigenkets of the operator α, a_n s being the corresponding eigenvalues. It can be easily seen that $c \mid A_n \rangle$ (where c is an arbitrary complex number) is also an eigenket belonging to the same eigenvalue a_n. Now, if there is more than one ket (and they are not linearly dependent on each other*) belonging to the same eigenvalue, i.e., if

$$\alpha \mid A_1 \rangle = a_1 \mid A_1 \rangle \tag{28}$$

$$\alpha \mid A_2 \rangle = a_1 \mid A_2 \rangle \tag{29}$$

then the state is said to be a degenerate state (cf. discussion in Sec. 3.3). If there are g linearly independent kets belonging to the same eigenvalue then the state is said to be g-fold degenerate. For the sake of simplicity, let us consider a 2-fold degenerate state described by Eqs. (28) and (29). If we multiply Eq. (28) by c_1 and Eq. (29) by c_2 and add we would get

$$\alpha \mid P \rangle = a_1 \mid P \rangle, \quad \mid P \rangle = c_1 \mid A_1 \rangle + c_2 \mid A_2 \rangle$$

implying that the linear combination $c_1 \mid A_1 \rangle + c_2 \mid A_2 \rangle$ is also an eigenket belonging to the same eigenvalue. Similarly, one can discuss a g-fold degenerate state.

When α is *real*, it can easily be shown that all the eigenvalues are real and for two different eigenvalues (i.e., for $a_n \neq a_m$) the corresponding eigenfunctions are necessarily orthogonal, i.e.,

$$\langle A_n \mid A_m \rangle = 0 \qquad \text{for} \qquad a_n \neq a_m \tag{30}$$

Further, one can always normalize the kets and choose appropriate linear combination for the kets belonging to a degenerate state such that (see Problem 3.3)

$$\langle A_n \mid A_m \rangle = \delta_{nm} \tag{31}$$

**

The proof is very simple. Premultiplying Eq. (27) by $\langle A_n \mid$ we get

$$\langle A_n \mid \alpha \mid A_n \rangle = a_n \langle A_n \mid A_n \rangle$$

---

*A ket $\mid P \rangle$ is said to be linearly dependent on the kets $\mid A_1 \rangle, \mid A_2 \rangle \ldots$ and $\mid A_P \rangle$ if we can write

$$\mid P > = \sum_{n=1}^{P} c_n \mid A_n >$$

**Equation (31) is strictly true for discrete states. For states belonging to continuum the Kronecker delta function is replaced by the Dirac delta function (see Eq. 42, Problems 8.1 and 8.2).

Now $\langle A_n \mid A_n \rangle$ is always real and not a null ket [otherwise Eq. (27) has no meaning]. Further, since α is real

$$\langle A_n \mid \alpha \mid A_n \rangle = \langle A_n \mid \bar{\alpha} \mid A_n \rangle = \overline{\langle A_n \mid \alpha \mid A_n \rangle}$$

implying that $\langle A_n \mid \alpha \mid A_n \rangle$ is also real and hence a_n must be real. Further, in order to prove Eq. (30) we consider

$$\alpha \mid A_1 \rangle = a_1 \mid A_1 \rangle \tag{32}$$

$$\alpha \mid A_2 \rangle = a_2 \mid A_2 \rangle \tag{33}$$

If we put $\mid P \rangle = \alpha \mid A_2 \rangle$, then $\langle P \mid = \langle A_2 \mid \bar{\alpha} = \langle A_2 \mid \alpha$; also $\langle P \mid = \bar{a}_2 \langle A_2 \mid = a_2 \langle A_2 \mid$ because a_2 is real. Thus

$$\langle A_2 \mid \alpha = a_2 \langle A_2 \mid \tag{34}$$

Premultiplying Eq. (32) by $\langle A_2 \mid$ and postmultiplying Eq. (34) by $\mid A_1 \rangle$ gives

$$\langle A_2 \mid \alpha \mid A_1 \rangle = a_1 \langle A_2 \mid A_1 \rangle = a_2 \langle A_2 \mid A_1 \rangle$$

which immediately gives the orthogonality condition given by Eq. (30). Equation (31) follows from Problem 3.3.

Since the formalism is symmetrical with respect to bras and kets we also have the eigenvalue equation

$$\langle B_n \mid \alpha = \langle B_n \mid b_n = b_n \langle B_n \mid$$

where $\langle B_n \mid$ are the eigenbras and b_n the corresponding eigenvalues. It can be easily seen that when α is a real operator and if $\mid A \rangle$ is an eigenket then $\langle A \mid$ is an eigenbra belonging to the same eigenvalue.

8.5 Observables

Any dynamical quantity (like the position co-ordinates, or components of the momentum or angular momentum, etc.) that can be measured is known as an observable. We assume that observables can be represented by linear operators and the operators corresponding to different observables need not commute. Further, the result of measurement of any observable must be an eigenvalue of the operator corresponding to the observable and since the measured value must be a real number we assume that the corresponding operator must be real.

Let us assume that a dynamical system is in a state which is an eigenket of the observable α belonging to the eigenvalue α'. Now, if a measurement of the observable α is made then it is certain that the value α' will be obtained. On the other hand, if the system is in a state described by the normalized ket

$$\mid P \rangle = c_1 \mid \alpha' \rangle + c_2 \mid \alpha'' \rangle$$

$\langle P \mid P \rangle = 1$) then a measurement of α would lead either to α' or α'' with probabilities $|c_1|^2$ and $|c_2|^2$ respectively. Since $\langle P|P\rangle = 1$, it immediately follows that

$$|c_1|^2 + |c_2|^2 = 1 \tag{35}$$

In general, if the system is in an arbitrary state then a measurement of α will make the dynamical system jump to one of the eigenstates of α. We further assume that the possible eigenstates of α to which the dynamical system may jump are such that the original state should be linearly expressible in terms of the eigenstates. Thus, any state can be expressed as a linear combination of the eigenkets of the observable and thus the eigenkets of an observable must form a complete set.

A beautiful example of the above argument is the famous Stern-Gerlach experiment (see Sec. 1.9, 9.4–9.6) where an inhomogeneous magnetic field (in the z-direction) splits the silver beam into two components, one going in the $+z$ direction and the other going in the $-z$ direction; the experiment tries to make a measurement of the z-component of the angular momentum (which we denote by M_z) and the result shows that M_z has only two eigenvalues. If one of the components of the beam is again passed through a similar inhomogeneous field (in the z-direction) then no further splitting will occur because the system is already in an eigenstate of M_z. However, if this beam was passed through an inhomogeneous field in the x-direction then the beam would split into two components of equal intensity because

$$|z\uparrow\rangle = \frac{1}{\sqrt{2}}[|x\uparrow\rangle + |x\downarrow\rangle]$$

where $|z\uparrow\rangle$ and $|z\downarrow\rangle$ are the (normalized) eigenkets of M_z and $|x\uparrow\rangle$ and $|x\downarrow\rangle$ are the eigenkets of M_x (see Sec. 9.4). Thus if the system is in the $|z\uparrow\rangle$ state (i.e., in an eigenstate of M_z) and if M_x is measured then the probabilities of obtaining the up (or down) state is 1/2.

8.6 The Completeness Condition

We have just stated that the eigenkets of an observable form a complete set. Let $|n\rangle$, $n = 0, 1, 2 \ldots$ denote these eigenkets and let $|P\rangle$ denote an arbitrary ket. Thus

$$|P\rangle = \sum c_n |n\rangle$$

where Σ denotes a sum over the discrete states and an integration over the continuum states. Since the eigenkets form an orthonormal set ($\langle m|n\rangle = \delta_{mn}$) we have

$$\langle m|P\rangle = \sum_n c_n \langle m|n\rangle = \sum_n c_n \delta_{mn} = c_m$$

Thus

$$|P\rangle = \sum_n |n\rangle c_n = \Big\{\sum_n |n\rangle\langle n|\Big\}|P\rangle \tag{36}$$

Since the above equation holds for an arbitrary ket $|P\rangle$, the quantity inside the curly brackets must be an unit operator

$$\sum_n |n\rangle\langle n| = 1 \tag{37}$$

which is usually referred to as the completeness condition. For states belonging to a continuum the sum is replaced by an integral [see Eqs. (40) and (47)].

8.7 Examples from Matrix Algebra

The bras and kets follow the same axiomatic rules as row and column matrices whereas linear operators follow the axiomatic rules of a square matrix. Thus, as an example of the formalism developed in Secs. 8.2–8.6, we consider the following square matrix and denote it by α

$$\alpha = \begin{bmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 2 \end{bmatrix}$$

We have assumed α to be a 3×3 matrix; we could have assumed it to be of an arbitrary order. Let

$$|A\rangle = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} \quad \text{and} \quad |B\rangle = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix}$$

denote two arbitrary column vectors in the same field (i.e., having 3 rows). Obviously

$$\langle A| = (\bar{a}_1\,\bar{a}_2\,\bar{a}_3) \qquad \text{and} \quad \langle B| = (\overline{b_1}\;\overline{b_2}\;\overline{b_3})$$

It is easy to see that $\langle A|A\rangle \geqslant 0$, the equality sign will occur only when $a_1 = a_2 = a_3 = 0$ which will represent the null ket. Further, the scalar products $\langle A|B\rangle$ or $\langle B|A\rangle$ are just numbers and $\langle A|B\rangle = \overline{\langle B|A\rangle}$. The multiplication $\alpha\,|A\rangle$ would give another column matrix, i.e., a ket vector, and the multiplication $\langle A|\,\alpha$ would give a row matrix, i.e., a bra vector. The operations $\alpha\langle A|$ and $|A\rangle\alpha$ are meaningless. Further, for the chosen form of α

$$\langle A|\alpha|B\rangle = \overline{\langle B|\alpha|A\rangle}$$

showing $\alpha = \bar{\alpha}$ and therefore α is a real or Hermitian matrix. All square matrices for which $\alpha_{ij} = \bar{\alpha}_{ji}$ are Hermitian matrices. The eigenvalues of α are 2, 1,

-1 (all real) and the corresponding eigenvectors are

$$|1\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, |2\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ i \\ 0 \end{bmatrix} \text{ and } |3\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -i \\ 0 \end{bmatrix}$$

They form an orthonormal set of kets in the sense that $\langle n | m \rangle = \delta_{nm}$. Further, an arbitrary ket can be expanded in terms of the eigenkets; thus

$$|A\rangle = a_3 |1\rangle + \frac{1}{\sqrt{2}}(a_1 - ia_2)|2\rangle + \frac{1}{\sqrt{2}}(a_1 + ia_2)|3\rangle$$

The multiplication of a column matrix and a row matrix, i.e., $|A\rangle\langle B|$ will give a sqaure matrix and hence is equivalent to a linear operator and it is easy to show that

$$\sum_n |n\rangle\langle n| = |1\rangle\langle 1| + |2\rangle\langle 2| + |3\rangle\langle 3| = 1$$

[cf. Eq. (37)]; here the unity on the right hand side represents a unit 3 × 3 matrix.

Finally, two square matrices need not commute, i.e., in general $\alpha\beta \neq \beta\alpha$.

8.8 Relationship between Kets and Wavefunctions

We shall now develop a relationship between the description of the states of a particle in terms of the Schrödinger wavefunctions (see Chapters 3 and 5) and the bra and ket vectors developed in this chapter. For the sake of simplicity we will restrict our considerations to one dimensional problems, the corresponding three dimensional generalizations are quite straightforward (see Problem 8.18). Let $|\Psi\rangle$ and $|\Phi\rangle$ represent the kets corresponding to the states described by the wavefunctions $\psi(x)$ and $\varphi(x)$ respectively; their scalar products are defined to be equal, i.e.,

$$\langle \Phi | \Psi \rangle = \int \varphi^*(x)\, \psi(x)\, dx = \overline{\langle \Psi | \Phi \rangle} \tag{38}$$

Let $|x'\rangle$ represent the state in which the particle is localized at the point x'; the corresponding eigenfunction is $\delta(x - x')$ (see Problem 8.1). Thus

$$\langle x' | \Psi \rangle = \int \delta(x - x')\, \psi(x) dx = \psi(x')$$

or

$$\psi(x) = \langle x | \Psi \rangle \tag{39}$$

Now

$$\langle \Phi \mid \Psi \rangle = \int dx\, \varphi^*(x)\, \psi(x) = \int dx\, \overline{\langle x \mid \Phi \rangle}\, \langle x \mid \Psi \rangle$$

$$= \int dx\, \langle \Phi \mid x \rangle \langle x \mid \Psi \rangle$$

$$= \langle \Phi \mid \left\{ \int dx \mid x \rangle \langle x \mid \right\} \mid \Psi \rangle$$

Since the above equation holds for arbitrary $\mid \Psi \rangle$ and $\mid \Phi \rangle$ the quantity inside the curly bracket must be an unit operator, i.e.,

$$\int dx \mid x \rangle \langle x \mid = 1 \tag{40}$$

which is nothing but the completness condition [cf. Eq. (37)]. the summation is however replaced by an integral because the states form a continuum. Using Eq. (40), an arbitrary ket can be written as the continuous form of Eq. (36), i.e.,

$$\mid \Psi \rangle = \int dx \mid x \rangle \langle x \mid \Psi \rangle = \int dx\, \psi(x) \mid x \rangle \tag{41}$$

which is also known as the spectral theorem (see Bohm, 1979). Now

$$\psi(x) = \langle x \mid \Psi \rangle = \int dx'\, \psi(x') \langle x \mid x' \rangle$$

which immediately gives [see Eq. (3) of Appendix F]

$$\langle x \mid x' \rangle = \delta(x - x') \tag{42}$$

This is the orthornormality condition [cf. Eq. (31), see also Problems 8.1 and 8.2].

We next consider the eigenkets corresponding to the momentum operator p_{op}:

$$p_{op} \mid p \rangle = p \mid p \rangle \tag{43}$$

where the eigenvalue p on the right hand side is just a number. Now, the eigenfunctions of the momentum operator are given by (see Problem 8.2)

$$\langle x \mid p \rangle = \psi_p(x) = \frac{1}{(2\pi\hbar)^{1/2}} \exp\,[ipx/\hbar] \tag{44}$$

Further, an arbitrary function can be written as [see Eq. (63) of Chapter 2]

$$\psi(x) = \int a(p)\, \psi_p(x)\, dp = \frac{1}{(2\pi\hbar)^{1/2}} \int_{-\infty}^{+\infty} a(p)\, e^{ipx/\hbar}\, dp \tag{45}$$

Thus

$$a(p) = \frac{1}{(2\pi\hbar)^{1/2}} \int \psi(x)\, e^{-ipx/\hbar}\, dx = \int \langle x \mid \Psi \rangle\, \overline{\langle x \mid p \rangle}\, dx$$

$$= \langle p \mid \left\{ \int dx \mid x \rangle \langle x \mid \right\} \mid \Psi \rangle$$

$$= \langle p \mid \Psi \rangle \qquad \text{[using Eq. (40)]}$$

and

$$\langle x \mid \Psi \rangle = \psi(x) = \int_{-\infty}^{+\infty} \psi_p(x)\, a(p) dp = \langle x \mid \left\{ \int dp \mid p \rangle \langle p \mid \right\} \mid \Psi \rangle \tag{46}$$

which gives the completeness condition [cf. Eqs. (37) and (40)]

$$\int dp \mid p \rangle \langle p \mid = 1 \tag{47}$$

Premultiplying by $\langle x' \mid$ and postmultiplying by $\mid x \rangle$ we get

$$\int dp \langle x' \mid p \rangle \langle p \mid x \rangle = \langle x' \mid x \rangle = \delta(x - x')$$

or

$$\frac{1}{2\pi\hbar} \int e^{ip(x'-x)/\hbar}\, dp = \delta(x - x')$$

which is the orthonormality condition (see also Problem 8.2). One can now see the point of introducing the abstract entity of a ket (or bra) to represent the state of a system. The wavefunction in coordinate space $\psi(x)$ can be regarded as the projection of the ket $\mid \Psi \rangle$ on the coordinate axis and the wavefunction in momentum space as the projection of $\mid \Psi \rangle$ on the momentum axis. On the other hand, one can carry out manipulations without reference to a representation using the ket.

8.9 The Linear Harmonic Oscillator Problem

We illustrate the use of the Dirac bra and ket algebra by solving the important problem of the linear harmonic oscillator which has already been discussed in in Sec. 3.6.3 by another method. The Hamiltonian is given by

$$H = \frac{1}{2m} \left[p^2 + \frac{1}{2} m\omega^2 x^2 \right] \tag{48}$$

Our objective is to solve the eigenvalue equation

$$H \mid H' \rangle = H' \mid H' \rangle \tag{49}$$

where $\mid H' \rangle$ is an eigenket of the operator H belonging to the eigenvalue H'.

The basic assumption will be the commutation relation*

$$[x, p] = xp - px = i\hbar \tag{50}$$

(see Sec. 2.3) which will be considered here as an axiom.

In order to solve the eigenvalue problem, we introduce the operator a and its adjoint $\bar{a}$ through the equations

$$a = \frac{1}{(2m\hbar\omega)^{1/2}}(m\omega x + ip) \tag{51}$$

and

$$\bar{a} = \frac{1}{(2m\hbar\omega)^{1/2}}(m\omega x - ip) \tag{52}$$

where we have used the fact that x and p are observables and hence $\bar{x} = x$ and $\bar{p} = p$. In terms of the above operators

$$\begin{aligned} \hbar\omega a\bar{a} &= \frac{1}{2m}(m\omega x + ip)(m\omega x - ip) \\ &= \frac{1}{2m}[m^2\omega^2x^2 + p^2 - im\omega(xp - px)] \\ &= H + \frac{1}{2}\hbar\omega \end{aligned} \tag{53}$$

where we have used Eqs. (48) and (50). Similarly

$$\hbar\omega\bar{a}a = H - \frac{1}{2}\hbar\omega \tag{54}$$

Thus

$$H = \frac{1}{2}\hbar\omega(\bar{a}a + a\bar{a}) \tag{55}$$

and

$$a\bar{a} - \bar{a}a = [a, \bar{a}] = 1 \tag{56}$$

From Eq. (53)

$$\omega a\bar{a}a = Ha + \frac{1}{2}\hbar\omega a \tag{57}$$

and from Eq. (54)

$$\hbar\omega\, a\bar{a}\, a = aH - \frac{1}{2}\hbar\omega a \tag{58}$$

Thus

$$aH - Ha = [a, H] = \hbar\omega a \tag{59}$$

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*In a similar manner when we consider the angular momentum problem using the bra and ket algebra, the basic equation will be the commutation relation (see Chapter 9).

Similarly

$$\bar{a}H - H\bar{a} = [\bar{a}, H] = -\hbar\omega\bar{a} \tag{60}$$

Let

$$|P\rangle = a\,|H'\rangle$$

where $|H'\rangle$ is an eigenket of H belonging to the eigenvalue H' [see Eq. (49)]. Then

$$\begin{aligned}\hbar\omega\langle P\,|\,P\rangle &= \hbar\omega\,\langle H'\,|\,\bar{a}a\,|\,H'\rangle\\ &= \langle H'\,|\,H - \frac{1}{2}\,\hbar\omega\,|\,H'\rangle \qquad \text{[using Eq. (54)]}\\ &= \left(H' - \tfrac{1}{2}\hbar\omega\right)\langle H'\,|\,H'\rangle \quad \text{[using Eq. (49)]}\end{aligned}$$

But $\langle P\,|\,P\rangle$ and $\langle H'\,|\,H'\rangle$ are positive numbers [see Eq. (6)] and therefore

$$H' \geqslant \tfrac{1}{2}\,\hbar\omega \tag{61}$$

the equality sign occurring (i.e., $H' = \frac{1}{2}\,\hbar\omega$) if and only if $|\,P\rangle = a\,|\,H'\rangle = 0$. (Conversely, $a\,|\,H'\rangle$ is a null ket only when the $H' = \frac{1}{2}\,\hbar\omega$). That all eigenvalues of H should be positive also follows from Eq. (48) and the fact that the expectation values of x^2 and p^2 should be positive. Next, let us consider the operator Ha acting on $|\,H'\rangle$

$$\begin{aligned}Ha\,|\,H'\rangle &= [aH - \hbar\omega a]\,|\,H'\rangle \quad \text{[using Eq. (59)]}\\ &= (aH' - \hbar\omega a)\,|\,H'\rangle\\ &= (H' - \hbar\omega)\,a\,|\,H'\rangle\end{aligned} \tag{62}$$

The above equation tells us that if $|\,H'\rangle$ is an eigenket of H then $a\,|\,H'\rangle$ is also an eigenket of H belonging to the eigenvalue $(H' - \hbar\omega)$ provided of course $a\,|\,H'\rangle$ is not a null ket which will occur only if $H' = \frac{1}{2}\,\hbar\omega$. Thus if $H' \neq \frac{1}{2}\,\hbar\omega$, $H' - \hbar\omega$ is also an eigenvalue (provided $a\,|\,H'\rangle \neq 0$) and similarly $H' - 2\hbar\omega$, $H' - 3\hbar\omega, \ldots$, etc. are also eigenvalues provided $aa\,|\,H'\rangle$, $aaa\,|\,H'\rangle, \ldots$ are not null kets. This, however, cannot go on indefinitely because it will then contradict Eq. (61). Further, it can terminate only at $H' = \frac{1}{2}\hbar\omega$ because then $a\,|\,E_0\rangle = 0$, $(E_0 = \frac{1}{2}\hbar\omega)$.

In a similar manner,

$$\begin{aligned}H\bar{a}\,|\,H'\rangle &= (\bar{a}H + \hbar\omega\bar{a})\,|\,H'\rangle \quad \text{[using Eq. (60)]}\\ &= (H' + \hbar\omega)\,\bar{a}\,|\,H'\rangle\end{aligned}$$

implying that if $|\,H'\rangle$ is an eigenket of H then $\bar{a}\,|\,H'\rangle$ is also an eigenket of H belonging to the eigenvalue $H' + \hbar\omega$ provided $\bar{a}\,|\,H'\rangle$ is not a null ket; this, however, can never happen because it would give

$$\begin{aligned}0 = \hbar\omega\,\langle H'\,|\,a\bar{a}\,|\,H'\rangle &= \langle H'\,|\,H + \tfrac{1}{2}\hbar\omega\,|\,H'\rangle \quad \text{[using Eq. (53)]}\\ &= (H' + \tfrac{1}{2}\hbar\omega)\,\langle H'\,|\,H'\rangle\end{aligned}$$

implying that $H' = -\frac{1}{2}\hbar\omega$ which is an impossibility because of Eq. (61) and $| H' \rangle$ by definition is not a null ket. Thus if H' is an eigenvalue than $H' + \hbar\omega$ is *always* another eigenvalue and since the eigenvalues must terminate at $\frac{1}{2}\hbar\omega$, we have

$$H' = E_n = (n + \tfrac{1}{2}\hbar\omega) \quad n = 0, 1, 2, 3 \dots \tag{63}$$

as the eigenvalues of H which is the same result as obtained in Sec. 3.6.3. We denote the eigenket belonging to the eigenvalue $(n + \frac{1}{2})\,\hbar\omega$ as $| n \rangle$; thus the eigenvalue equation is

$$H \,|\, n \rangle = (n + \tfrac{1}{2})\,\hbar\omega \,|\, n \rangle; \quad n = 0, 1, 2, \dots \tag{64}$$

We assume that the eigenkets are normalized so that

$$\langle m \,|\, n \rangle = \delta_{mn} \tag{65}$$

Now, $a \,|\, n \rangle$ is an eigenket of H belonging to the eigenvalue $(n - \frac{1}{2})\hbar\omega$, thus $a \,|\, n \rangle$ must be a multiple of $| \, n - 1 \rangle$

$$a \,|\, n \rangle = \alpha_n \,|\, n - 1 \rangle$$

Obviously for the ground state

$$a \,|\, 0 \rangle = 0 \tag{66}$$

In order to determine α_n we calculate the square of the length of $a \,|\, n \rangle$

$$\langle n \,|\, \bar{a} a \,|\, n \rangle = |\, \alpha_n \,|^2 \langle n - 1 \,|\, n - 1 \rangle = |\, \alpha_n \,|^2$$

But

$$\begin{aligned} \hbar\omega \,\langle n \,|\, \bar{a} a \,|\, n \rangle &= \langle n \,|\, (H - \tfrac{1}{2}\hbar\omega) \,|\, n \rangle \\ &= \langle n \,|\, (n + \tfrac{1}{2})\hbar\omega - \tfrac{1}{2}\hbar\omega \,|\, n) \\ &= n\hbar\omega \,\langle n \,|\, n \rangle = n\hbar\omega \end{aligned}$$

Thus

$$|\, \alpha_n \,|^2 = n$$

and therefore

$$a \,|\, n \rangle = \sqrt{n} \,|\, n - 1 \rangle \tag{67}$$

Similarly

$$\bar{a} \,|\, n \rangle = \sqrt{n + 1} \,|\, n + 1 \rangle \tag{68}$$

Thus, if $| \, 0 \rangle$ denotes the ground state eigenket, then

$$| 1 \rangle = \frac{\bar{a}}{\sqrt{1}} \,| 0 \rangle; \quad | 2 \rangle = \frac{\bar{a}\bar{a}}{\sqrt{1}\sqrt{2}} \,| 0 \rangle = \frac{\bar{a}^2}{\sqrt{2!}} \,| 0 \rangle$$

$$| 3 \rangle = \frac{(\bar{a})^3}{\sqrt{3!}} \,| 0 \rangle \dots$$

and, in general

$$| n \rangle = \frac{\bar{a}^n}{\sqrt{n!}} \, | 0 \rangle \tag{69}$$

If we assume that the state corresponding to $| n \rangle$ contains n quanta of energy then the operator $\bar{a}$ creates a quantum of energy and the operator a annihilates a quantum of energy. For this reason $\bar{a}$ and a are often referred to as creation and annihilation operators respectively (see also Chapter 22). The matrix representation of various operators are discussed in Problem 8.7.

8.9.1 The Uncertainty Product

In this section we will calculate the uncertainty product $\Delta x \, \Delta p$ for the harmonic oscillator problem. The uncertainties Δx and Δp are given by (see Sec. 2.6)

$$\Delta x = [\langle x^2 \rangle - \langle x \rangle^2]^{1/2} \quad \text{and} \quad \Delta p = [\langle p^2 \rangle - \langle p \rangle^2]^{1/2} \tag{70}$$

Using Eqs. (51) and (52)

$$x = \left(\frac{\hbar}{2m\omega} \right)^{1/2} (\bar{a} + a) \tag{71}$$

$$p = i \left(\frac{m\hbar\omega}{2} \right)^{1/2} (\bar{a} - a) \tag{72}$$

Thus

$$\begin{aligned} \langle x \rangle = \langle n | x | n \rangle &= \left(\frac{\hbar}{2m\omega} \right)^{1/2} \langle n | \bar{a} + a | n \rangle \\ &= \left(\frac{\hbar}{2m\omega} \right)^{1/2} [\sqrt{n+1} \, \langle n | n+1 \rangle + \sqrt{n} \, \langle n | n-1 \rangle] \\ &\qquad\qquad\qquad\qquad \text{[using Eqs. (67) and (68)]} \\ &= 0 \end{aligned}$$

and

$$\begin{aligned} \langle x^2 \rangle = \langle n | x^2 | n \rangle &= \frac{\hbar}{2m\omega} [\langle n | aa | n \rangle + \langle n | a\bar{a} | n \rangle \\ &\qquad + \langle n | \bar{a}a | n \rangle + \langle n | \bar{a}\bar{a} | n \rangle] \\ &= \frac{\hbar}{2m\omega} [0 + (n+1) + n + 0] = (n + \tfrac{1}{2}) \hbar / m\omega \end{aligned} \tag{73}$$

Similarly

$$\langle p \rangle = \langle n | p | n \rangle = 0 \quad \text{and} \quad \langle p^2 \rangle = m\omega\hbar \, (n + \tfrac{1}{2}) \tag{74}$$

giving

$$\Delta x \, \Delta p = (n + \tfrac{1}{2}) \hbar \tag{75}$$

the minimum value ($= \frac{1}{2}\hbar$) occurring for the ground state (see Sec. 2.6, Problems 2.20 and 3.8).

8.9.2. THE HARMONIC OSCILLATOR WAVEFUNCTIONS

Using Eq. (66) we get

$$0 = \langle x \mid a \mid 0 \rangle = \frac{1}{(2m\hbar\omega)^{1/2}} \langle x \mid m\omega x + ip \mid 0 \rangle$$
$$= \left[\left(\frac{m\omega}{2\hbar} \right)^{1/2} x + \left(\frac{2\hbar}{m\omega} \right)^{1/2} \frac{d}{dx} \right] \psi_0 \qquad (76)$$

where $\psi_0 = \langle x \mid 0 \rangle$ and we have used the relation (see Problem 8.17)

$$\langle x \mid p \mid 0 \rangle = -i\hbar \frac{d}{dx} \langle x \mid 0 \rangle = -i\hbar \frac{d\psi_0}{dx} \qquad (77)$$

Equation (77) can be immediately integrated to give $\psi_0 \sim \exp[-m\omega x^2/2\hbar]$ and normalizing it we get [cf. Eq. (72) of Chapter 3]

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp\left[-\frac{m\omega}{2\hbar} x^2 \right] \qquad (78)$$

Now

$$\psi_1 = \langle x \mid 1 \rangle = \langle x \mid \bar{a} \mid 0 \rangle = \frac{1}{(2m\hbar\omega)^{1/2}} \langle x \mid m\omega x - ip \mid 0 \rangle$$
$$= \frac{1}{(2m\hbar\omega)^{1/2}} \left[m\omega x \psi_0 - \hbar \frac{d\psi_0}{dx} \right] = \left(\frac{2m\omega}{\hbar} \right)^{1/2} x\psi_0 \qquad (79)$$

Similarly, we can calculate ψ_2, ψ_3, etc. and will get expressions identical to the one given by Eq. (72) of Chapter 3. It may be noted that in the present analysis since ψ_0 has been normalized, ψ_1, ψ_2, ψ_3 will automatically be normalized.

8.9.3 THE COHERENT STATES

Consider the eigenvalue equation

$$a \mid \alpha \rangle = \alpha \mid \alpha \rangle \qquad (80)$$

where a is the annihilation operator defined through Eq. (51). The eigenkets defined by Eq. (80) are known as the coherent states*. In this section we will study some of the properties of the coherent states which are of great importance in quantum theory of radiation (see Chapter 22).

Since the eigenkets of an observable form a complete set, we expand $\mid \alpha \rangle$ in terms of the kets $\mid n \rangle$

$$\mid \alpha \rangle = \sum_n c_n \mid n \rangle$$

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*It is of interest to mention that when a laser is operated much beyond the threshold, it generates a coherent state excitation of the cavity mode; see, e.g., Loudon (1973), Thyagarajan and Ghatak (1981).

Now

$$a\,|\,\alpha\rangle = \sum c_n a\,|\,n\rangle = \sum_{n=1}^{\infty} c_n n^{1/2}\,|\,n-1\rangle \tag{81}$$

Also

$$a\,|\,\alpha\rangle = \alpha\,|\,\alpha\rangle = \alpha \sum_n c_n\,|\,n\rangle \tag{82}$$

Equating Eqs. (81) and (82) we get

$$c_1 = \alpha c_0, \quad c_2 = \frac{\alpha c_1}{\sqrt{2}} = \frac{\alpha^2}{\sqrt{2!}}\,c_0, \ldots$$

or

$$|\,\alpha\rangle = c_0 \sum \frac{\alpha^n}{\sqrt{n!}}\,|\,n\rangle$$

If we normalize $|\,\alpha\rangle$, we would get

$$\langle\alpha\,|\,\alpha\rangle = |\,c_0\,|^2 \sum\sum \frac{\alpha^n \alpha^{*m}}{\sqrt{n!}\,\sqrt{m!}}\,\delta_{nm} = |\,c_0\,|^2 \exp\,[\,|\,\alpha\,|^2]$$

or

$$|\alpha\rangle = \exp\left[-\frac{1}{2}\,|\,\alpha\,|^2\right] \sum_n \frac{\alpha^n}{\sqrt{n!}}\,|\,n\rangle \tag{83}$$

within an arbitrary phase factor. Notice that there is no restriction on the value of α; i.e., α can take any complex value. The coherent states play a very important role in the quantum theory of radiation, a brief account of which is given in Chapter 22; for a more detailed account the reader is referred to Louisell (1973). Some of the properties of the coherent states are discussed in Problems 8.19, 8.20, 8.22–8.24 and also in Secs. 22.5 and 22.6.

8.10 Simultaneous Eigenkets of Commuting Operators

Let α and β represent the operators corresponding to two observables. We assume that the two operators commute, i.e.,

$$\alpha\beta = \beta\alpha \tag{84}$$

Let $|\,\alpha'\rangle$ be an eigenket of α belonging to the eigenvalue α'

$$\alpha\,|\,\alpha'\rangle = \alpha'\,|\,\alpha'\rangle$$

then

$$\alpha\{\beta\,|\,\alpha'\rangle\} = \beta\alpha\,|\,\alpha'\rangle = \alpha'\{\beta\,|\,\alpha'\rangle\} \tag{85}$$

because α' is a number. Thus $\beta\,|\,\alpha'\rangle$ is also an eigenket of α belonging to the same eigenvalue α'. If $|\,\alpha'\rangle$ corresponds to a non-degenerate state then Eq. (85)

tells us that $\beta \mid \alpha' \rangle$ must be a multiple of $\mid \alpha' \rangle$, i.e.,

$$\beta \mid \alpha' \rangle = \beta' \mid \alpha' \rangle$$

where β' is a number. The above equation implies that $|\alpha'\rangle$ must be an eigenket of β. Hence, all the eigenkets of α which correspond to nondegenerate states, must also be eigenkets of β and hence these will be simultaneous eigenkets. On the other hand, if α' corresponds to a g-fold degenerate state then Eq. (85) tells us that $\beta \mid \alpha_k' \rangle$ must be expressible as a linear combination of $\mid \alpha_i' \rangle$

$$\beta \mid \alpha_k' \rangle = \sum_{i=1}^{g} c_{ki} \mid \alpha_i' \rangle \tag{86}$$

Now, the kets $\mid \alpha_i' \rangle$ need not be eigenkets of β; however, we may always choose appropriate linear combinations of $\mid \alpha_i' \rangle$ which are also eigenkets of β. Let the required linear combination be

$$\sum_{k=1}^{n} d_k \mid \alpha_k' \rangle$$

Thus we may impose

$$\beta \sum_{k=1}^{n} d_k \mid \alpha_k' \rangle = \beta' \sum d_k \mid \alpha_k' \rangle$$

or

$$\sum_k \sum_i d_k c_{ki} \mid \alpha_i' \rangle = \beta' \sum_k d_k \mid \alpha_k' \rangle$$

Since $\mid \alpha_i' \rangle$ form an orthonormal set, we must have

$$\sum_k d_k c_{ki} = \beta' d_i$$

or

$$\sum_k (c_{ki} - \beta' \delta_{ik})\, d_k = 0$$

For non-trivial solutions

$$\text{determinant} \mid c_{ki} - \beta' \delta_{ik} \mid = 0$$

which will give n values of β'; the corresponding values of d_k will give us the required linear combinations.

In Chapter 6 we have shown that L^2 commutes with L_x, L_y and L_z but L_x, L_y and L_z do not commute among themselves. Thus we may form a complete set of simultaneous eigenfunctions of L^2 and L_z which will, in general, not be eigenfunctions of L_x (or L_y). Similarly, we can construct simultaneous eigenfunctions of L^2 and L_x which are not eigenfunctions of L_y or L_z (see Problem 8.12). Thus all eigenfunctions of L_z (or L_x or L_y) are also eigenfunctions of L^2 but the converse is not true.

It should be mentioned that if α and β do not commute, a simultaneous eigenstate is not impossible but rather rare. For example, for an S state ($l = 0$) the action of L_x, L_y or L_z will give zero

$$L_x \mid S\rangle = L_y \mid S\rangle = L_z \mid S\rangle = 0 \tag{87}$$

implying that $\mid S\rangle$ is a simultaneous eigenstate of L_x, L_y and L_z belonging to the eigenvalue zero.

Finally, if two observables α and β form a complete set of simultaneous eigenkets (say $\alpha \mid n\rangle = \alpha_n \mid n\rangle$ and $\beta \mid n\rangle = \beta_n \mid n)\rangle$ then for an arbitrary ket $\mid P\rangle$

$$(\alpha\beta - \beta\alpha) \mid P\rangle = (\alpha\beta - \beta\alpha) \sum c_n \mid n\rangle = \sum c_n(\alpha_n\beta_n - \alpha_n\beta_n) \mid n\rangle = 0$$

implying that α and β must commute [see Eq. (9)].

8.11 The Unitary Transformation

Let $\mid \Psi_i\rangle$ represent a set of orthonormal kets, i.e.,

$$\langle \Psi_i \mid \Psi_j\rangle = \delta_{ij}$$

We consider a transformation

$$\mid \Phi_i\rangle = \sum_j U_{ij} \mid \Psi_j \tag{88}$$

If the kets $\mid \Phi_i\rangle$ also form a set of orthonormal kets, i.e., if $\langle \Phi_i \mid \Phi_j\rangle = \delta_{ij}$ then the transformation is said to be unitary and U_{ij} is said to be a unitary matrix. Now

$$\begin{aligned}
\delta_{ij} = \langle \Phi_i \mid \Phi_j\rangle &= \sum_m \sum_n \overline{U}_{im}\, U_{in} \langle \Psi_m \mid \Psi_n\rangle \\
&= \sum_m \sum_n \overline{U}_{im}\, U_{jn}\, \delta_{mn} \\
&= \sum_n \overline{U}_{in}\, U_{jn}
\end{aligned}$$

or

$$\overline{U}U = 1 \tag{89}$$

where $\overline{U}$ represents the Hermitian adjoint of U. Thus if U describes a unitary transformation then

$$\overline{U} = U^{-1}$$

8.12 The Schrödinger and Heisenberg Pictures

While solving the linear harmonic oscillator problem in Sec. 8.9, we had assumed the observables x, p and H to be real operators and independent of time. This is the so-called Schrödinger picture and the time development of the ket describing the quantum mechanical system is obtained by solving the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = H \mid \Psi(t)\rangle \tag{90}$$

If the Hamiltonian is independent of time, we can 'integrate' the above equation to obtain

$$\mid \Psi(t)\rangle = e^{-iHt/\hbar} \mid \Psi(0)\rangle \tag{91}$$

where the exponential of an operator is *defined* through the power series

$$e^{\mathcal{O}} = 1 + \mathcal{O} + \frac{1}{2!}\mathcal{O}.\,\mathcal{O} + \frac{1}{3!}\mathcal{O}.\mathcal{O}.\mathcal{O} + \cdots \tag{92}$$

That Eq. (91) is the solution of Eq. (90) can be immediately seen by direct substitution. Next, let $\mid n\rangle$ represent the eigenkets of H

$$H \mid n\rangle = E_n \mid n\rangle$$

then by inserting the unit operator [see Eq. (37)] in Eq. (91) we obtain

$$\begin{aligned} \mid \Psi(t)\rangle &= e^{-iHt/\hbar}\left\{\sum_n \mid n\rangle\,\langle n \mid\right\} \mid \Psi(0)\rangle \\ &= \sum_n e^{-iE_nt/\hbar} \mid n\rangle\Big[\langle n \mid \Psi(0)\rangle\Big] \end{aligned} \tag{93}$$

The above equation may be used to study the time development of states. Now, the expectation value of an observable characterized by the operator is $\mathcal{O}$ given by

$$\langle \mathcal{O}\rangle = \langle \Psi(t) \mid \mathcal{O} \mid \Psi(t)\rangle \tag{94}$$

If we substitute for $\mid \Psi(t)\rangle$ from Eq. (91), we would get

$$\begin{aligned} \langle \mathcal{O}\rangle &= \langle \Psi(0) \mid e^{iHt/\hbar}\,\mathcal{O}\,e^{-iHt/\hbar} \mid \Psi(0)\rangle \\ &= \langle \Psi(0) | \mathcal{O}_H(t) \mid \Psi(0)\rangle \end{aligned} \tag{95}$$

where the operator $\mathcal{O}_H(t)$ is defined by the following equation

$$\mathcal{O}_H(t) = e^{iHt/\hbar}\,\mathcal{O}\,e^{-iHt/\hbar} \tag{96}$$

Equations (94) and (95) tell us that the expectation values remain the same if we endow the operators $\mathcal{O}_H(t)$ with the entire time dependence but assume that the kets are time independent. This is known as the Heisenberg picture (and hence the suscript H) in which operators representing the observable change with time but the ket describing the system is time independent. On the other hand, in the Schrödinger picture [see Eqs. (93) and (94)], we may visualize the basis vectors (here $|\, n\rangle$) as a fixed set of vectors and $|\, \Psi(t)\rangle$ (describing the system) as moving.

From Eq. (96), we have,

$$\frac{d}{dt}\mathcal{O}_H(t) = e^{iHt/\hbar}\,\frac{\partial\mathcal{O}}{\partial t}\,e^{-iHt/\hbar} + \frac{i}{\hbar}\,e^{iHt/\hbar}\,[H\mathcal{O} - \mathcal{O}H]\,e^{-iHt/\hbar}$$

where $\partial\mathcal{O}/\partial t$ is introduced to allow for any explicit time dependence of the operator. If there is no such explicit time dependence, we may write

$$\begin{aligned} i\hbar\frac{d}{dt}\mathcal{O}_H(t) &= [e^{iHt/\hbar}\,\mathcal{O}\,e^{-iHt/\hbar}]H \\ &\quad - H\,[e^{iHt/\hbar}\,\mathcal{O}\,e^{-iHt/\hbar}] \\ &= \mathcal{O}_H(t)H - H\mathcal{O}_H(t) \end{aligned}$$

or

$$i\hbar\,\frac{d}{dt}\mathcal{O}_H(t) = [\,\mathcal{O}_H(t), H] \tag{97}$$

Equation (97) gives the time dependence of an operator in the Heisenberg picture and is called the *Heisenberg equation of motion.* The Heisenberg equations of motion are widely used in literature; see, e.g., Problem 18.9.

If the Hamiltonian is assumed to be independent of time in the Schrödinger representation, then it is also independent of time in the Heisenberg representation

$$H_H(t) = e^{-iHt/\hbar}\,H\,e^{iHt/\hbar} = e^{-iHt/\hbar}\,e^{iHt/\hbar}\,H = H \tag{98}$$

It should be mentioned that if H had an explicit time dependence, the analysis would have been much more involved [see, e.g. Baym (1969) Chapter 5].

We next consider the operators α and β which, in the Schrödinger representation, satisfy the commutation relation

$$[\alpha, \beta] = i\gamma \tag{99}$$

or

$$\alpha\beta - \beta\alpha = i\gamma \tag{100}$$

If we multiply on the left by $e^{iHt/\hbar}$ and on the right be $e^{-iHt/\hbar}$, we obtain

$$\begin{aligned} &e^{iHt/\hbar}\alpha\,e^{-iHt/\hbar}\,e^{iHt/\hbar}\,\beta e^{-iHt/\hbar} - e^{iHt/\hbar}\,\beta e^{-iHt/\hbar}\,e^{iHt/\hbar}\,\alpha e^{-iHt/\hbar} \\ &= ie^{iHt/\hbar}\,\gamma\,e^{-iHt/\hbar} \end{aligned} \tag{101}$$

where we have inserted $e^{-iHt/\hbar}\,e^{\,iHt/\hbar}$ $(=1)$ between α and β. Using Eq. (96), we get

$$[\alpha_H(t), \beta_H(t)] = i\gamma_H(t) \tag{102}$$

which shows the physical equivalence of Heisenberg and Schrödinger pictures.

As an illustration we consider the harmonic oscillator problem. However, before we do so, we note that

$$[x, p^n] = i\hbar\, np^{n-1} = i\hbar \frac{\partial}{\partial p} p^n \tag{103}$$

and

$$[p, x^n] = -i\hbar\, nx^{n-1} = -i\hbar \frac{\partial}{\partial x} x^n \tag{104}$$

Thus if $P(p)$ and $X(x)$ can be expanded in a power series in p and x respectively we will have

$$[X, P(p)] = i\hbar \frac{\partial P}{\partial p} \tag{105}$$

and

$$[p, X(x)] = -i\hbar \frac{\partial X}{\partial x} \tag{106}$$

Now for the harmonic oscillator problem

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 = H_H = \frac{p_H^2(t)}{2m} + \frac{1}{2} m\omega^2 x_H^2(t) \tag{107}$$

where we have used Eq. (98). Thus, using Eq. (97)

$$\frac{d}{dt} x_H(t) = \frac{1}{i\hbar} [x_H, H_H] = \frac{\partial H_H}{\partial p} = \frac{p_H(t)}{m} \tag{108}$$

and

$$\frac{d}{dt} p_H(t) = \frac{1}{i\hbar} [p_H(t), H_H] = -\frac{\partial H_H}{\partial x} = -m\omega^2 x_H(t) \tag{109}$$

These are the Hamilton's equations of motion (see e.g., Goldstein, 1950). The solutions of the above equations are

$$x_H(t) = x \cos \omega t + \frac{p}{m\omega} \sin \omega t \tag{110}$$

$$p_H(t) = -m\omega x \sin \omega t + p \cos \omega t \tag{111}$$

where $x = x_H(t = 0)$ and $p = p_H(t = 0)$ represent the operators in the Schrödinger representation. Further,

$$\begin{aligned} a_H(t) &= \frac{1}{(2m\hbar\omega)^{1/2}} [m\omega x_H(t) + ip_H(t)] \\ &= a\, e^{-i\omega t} \end{aligned} \tag{112}$$

where $a = a_H(t = 0)$. Similarly

$$\bar{a}_H(t) = \bar{a}\, e^{i\omega t} \tag{113}$$

These relations will be used in Chapter 22.

8.13 The Interaction Picture

For completeness, we shall also introduce the interaction picture. Often, the Hamiltonian of a system of interest can be written as the sum of two parts

$$H = H_0 + H' \tag{114}$$

In such a division H_0 may, for example, represent the Hamiltonian of subsystems when interactions between them can be neglected; and H' the interaction itself. However, for the ensuing discussion, such an identification is not necessary. Starting with the Schrödinger picture, we have

$$i\hbar \frac{\partial}{\partial t} \mid \Psi_s \rangle = (H_0 + H') \mid \Psi_s \rangle \tag{115}$$

where the subscript s indicates that we are dealing with the Schrödinger picture. We introduce the interaction picture

$$\mid \Psi_{\text{int}} \rangle = e^{iH_0t/\hbar} \mid \Psi_s \rangle$$

or

$$\mid \Psi_s \rangle = e^{-iH_0t/\hbar} \mid \Psi_{\text{int}} \rangle \tag{116}$$

Substituting in Eq. (115), we obtain

$$i\hbar\, e^{-iH_0t/\hbar} \frac{\partial \mid \Psi_{\text{int}} \rangle}{\partial t} = H'\, e^{-iH_0t/\hbar} \mid \Psi_{\text{int}} \rangle \tag{117}$$

Multiplying by exp $iH_0t/\hbar$ on the left and writing

$$H'_{\text{int}} = e^{iH_0t/\hbar}\, H'\, e^{-iH_0t/\hbar} \tag{118}$$

we have the equation of motion in the interaction picture as

$$i\hbar \frac{\partial}{\partial t} \mid \Psi_{\text{int}} \rangle = H'_{\text{int}} \mid \Psi_{\text{int}} \rangle \tag{119}$$

In fact, all operators $\mathcal{O}$ change according to the rule (118), i.e.,

$$\mathcal{O}_{\text{int}} = e^{iH_0t/\hbar}\, \mathcal{O}\, e^{-iH_0t/\hbar} \tag{120}$$

Clearly, the interaction picture is a sort of intermediate case between the Schrödinger and Heisenberg pictures.

We see from Eqs. (96) and (120) that for any operator which commutes with the Hamiltonian, the operators in the Schrödinger and Heisenberg pictures are identical*; this means that in both cases the kets and the operators are time independent, so that the expectation values are constants of motion. A special case is that of the Hamiltonian itself (for an isolated system) for which we have

$$\frac{dH}{dt} = 0 \tag{121}$$

and the energy of the system is conserved.

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*This, of course, is true for the interaction picture as well.

8.14 The Density Operator

Let the kets $|0\rangle$, $|1\rangle$ $|2\rangle, \ldots |n\rangle, \ldots$ form a complete set of orthonormal kets; i.e.,

$$\sum_n |n\rangle\langle n| = 1 \tag{122}$$

and

$$\langle m|n\rangle = \delta_{mn} \tag{123}$$

An arbitrary ket $|P\rangle$ can be expanded in terms of the ket $|n\rangle$

$$|P\rangle = \sum_n c_n |n\rangle; \quad c_n = \langle n|P\rangle \tag{124}$$

A state can be characterized by the density operator ρ defined by the following equation

$$\rho = |P\rangle\langle P| \tag{125}$$

The trace* of an operator is defined to be equal to the sum of the diagonal matrix elements for any complete set of states; thus

$$\mathrm{Tr}\, \mathcal{O} = \sum_n \langle n|\mathcal{O}|n\rangle \tag{126}$$

Hence

$$\mathrm{Tr}(|P\rangle\langle Q|) = \sum_n \langle n|P\rangle\langle Q|n\rangle$$

$$= \langle Q|\left\{\sum_n |n\rangle\langle n|\right\}|P\rangle$$

or

$$\mathrm{Tr}(|P\rangle\langle Q|) = \langle Q|P\rangle \tag{127}$$

where in the last step we have used Eq. (37). Thus

$$\mathrm{Tr}\,\rho = \mathrm{Tr}\; |P\rangle\langle P| = \langle P|P\rangle = 1 \tag{128}$$

where we have assumed $|P\rangle$ to be normalized. Also

$$\rho_{nn} = \langle n|P\rangle\langle P|n\rangle = |c_n|^2$$

implying that the diagonal matrix elements of the density operator represent the probabilities of the system in the base states.

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*Abbreviated as Tr.

Now, the expectation value of the operator $\mathcal{O}$ is given by

$$\langle \mathcal{O} \rangle = \langle P \mid \mathcal{O} \mid P \rangle = \sum_n \langle P \mid \mathcal{O} \mid n \rangle \langle n \mid P \rangle \quad \text{[Using Eq. (122)]}$$

$$= \sum_n \langle n \mid P \rangle \langle P \mid \mathcal{O} \mid n \rangle \quad \text{[because } \langle n \mid P \rangle \text{ is a number]}$$

$$= \sum_n \langle n \mid \rho \mathcal{O} \mid n \rangle \quad \text{[using Eq. (125)]}$$

$$= \mathrm{Tr}\,(\rho \mathcal{O}) \tag{129}$$

Perhaps the most important application of the density operator is in the field of statistical machanics where we consider an ensemble of a large number of identical systems; each system may be in a different quantum state (see, e.g., Louisell, 1973). If W_Ψ represents the probability of finding the system in the state characterized by $\mid \Psi \rangle$, then the corresponding density operator is given by

$$\rho = \sum_\Psi w_\Psi \mid \Psi \rangle \langle \Psi \mid \tag{130}$$

where the summation is carried over all possible states of the system; the density operator contains all the information about the ensemble. Obviously, since

$$\sum_\Psi w_\Psi = 1 \tag{131}$$

we have

$$\mathrm{Tr}\,\rho = \sum_\Psi w_\Psi \,\mathrm{Tr} \mid \Psi \rangle \langle \Psi \mid$$

$$= \sum_\Psi w_\Psi \langle \Psi \mid \Psi \rangle \quad \text{[using Eq. (127)]}$$

$$= \sum_\Psi w_\Psi = 1 \tag{132}$$

As an example, we consider the radiation field at thermal equilibrium (at temperature T) inside a cavity. We will show in Chapter 22 that the radiation field can be visualized as consisting of an infinite number of simple harmonic oscillators. The energy of each oscillator can decrease or increase by integral multiples of $\hbar\omega_\lambda$; if we consider $\hbar\omega_\lambda$ as the energy of a photon, then each oscillator can have energy corresponding to n_λ photons. Restricting ourselves to a particular mode (i.e., to a particular frequency which we will denote by ω), the probability of finding n photons (i.e., the probability of finding the system in the nth excited state) is proportional to

$$\exp\left(-\frac{E_n}{kT}\right) = \exp\left[-\frac{\left(n+\frac{1}{2}\right)\hbar\omega}{kT}\right]$$

Thus

$$w_n = \frac{\exp\left[-\dfrac{\left(n+\dfrac{1}{2}\right)\hbar\omega}{kT}\right]}{\sum\limits_{n=0,1,\ldots}\exp\left[-\dfrac{\left(n+\dfrac{1}{2}\right)\hbar\omega}{kT}\right]} = \frac{\exp\left[-n\xi\right]}{1+e^{-\xi}+e^{-2\xi}+\ldots}$$

$$= \frac{e^{-n\xi}}{1/(1-e^{-\xi})} = e^{-n\xi}\left(1-e^{-\xi}\right) \tag{133}$$

where

$$\xi = \frac{\hbar\omega}{kT}$$

Thus

$$\rho = \left[1-e^{-\xi}\right]\sum_n e^{-n\xi}\,|\,n\rangle\,\langle n\,|$$

$$= \left[1-e^{-\xi}\right]\sum_n e^{-\xi\bar{a}a}\,|\,n\rangle\,\langle n\,| \quad \text{[because } \bar{a}a \text{ is the number operator,}$$

see Problem 8.9]

$$= \left[1-e^{-\xi}\right]e^{-\xi\bar{a}a}\sum_n |\,n\rangle\,\langle n\,|$$

or

$$\rho = \left[1-e^{-\xi}\right]e^{-\xi\bar{a}a} \tag{134}$$

The above equation can be put in the form

$$\rho = \frac{e^{-\beta H}}{\mathrm{Tr}\,(e^{-\beta H})},\ \beta = \frac{1}{kT}\ . \tag{135}$$

where H represents the Hamiltonian of the system.

PROBLEMS

PROBLEM 8.1

The equation

$$x\delta(x-x') = x'\delta(x-x') \tag{136}$$

suggests that the Dirac delta function $\delta(x-x')$ is an eigenfunction of the position operator x and the eigenvalues forming a continuous spectrum with $-\infty < x' < \infty$. Show that the eigenfunctions form a complete orthonormal set.

PROBLEM 8.2

Consider the eigenvalue equation of the momentum operator

$$p_{op}\psi_p = -i\hbar \frac{\partial}{\partial x}\psi_p = p\psi_p \tag{137}$$

where $p_{op}(= -i\hbar\, \partial/\partial x)$ is the operator representation of p_x (we are dropping the subscript x) and p (a number) represents the eigenvalue. Obtain the eigenvalue spectrum of p_{op} and show that the eigenfunctions form a complete orthonormal set. Generalize to three dimensions.

PROBLEM 8.3

Use Fourier series to show that the eigenfunctions in the particle in a box problem (see Sec. 3.6.1) form a complete orthonormal set.

PROBLEM 8.4

Using the completeness condition of the harmonic oscillator wavefunctions, prove that

$$\sum_n \psi_n^*(x')\,\psi_n(x) = \delta(x - x') \tag{138}$$

where $\psi_n(x)$ are given by Eq. (72) of Chapter 3.

PROBLEM 8.5

Prove that

$$\overline{|P\rangle\langle Q|} = |Q\rangle\langle P| \tag{139}$$

PROBLEM 8.6

Consider the linear operator σ defined by the equation

$$\sigma^2 = 1 \tag{140}$$

write the eigenvalue equation for σ and show that the eigenvalues of σ are ± 1. Also show that the kets $(1 \pm \sigma)\,|P\rangle$ (where $|P\rangle$ is an arbitrary ket) are eigenkets of σ belonging to the eigenvalues ± 1. Notice that an arbitrary ket can always be written as

$$|P\rangle = \frac{1}{2}\Big(1 + \sigma\Big)\,|P\rangle + \frac{1}{2}\Big(1 - \sigma\Big)\,|P\rangle \tag{141}$$

which shows that the eigenkets form a complete set.

PROBLEM 8.7*

In the harmonic oscillator problem express x and p in terms of a and $\bar{a}$ and calculate the following matrix elements

$$\langle m\,|\,x\,|\,n\rangle,\ \langle m\,|\,p\,|\,n\rangle \quad \text{and} \quad \langle m\,|\,H\,|\,n\rangle$$

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*Problems 8.7-8.11 correspond to the harmonic oscillator problem The operators a and $\bar{a}$ are everywhere the annihilation and creation operators.

and hence obtain matrix representations of x, p, H, a and $\bar{a}$ and show that whereas the matrices representing x, p and H are Hermitian, the matrices representing a and $\bar{a}$ are not Hermitian. Also show that

$$\langle n \mid \tfrac{1}{2} m\omega^2 x^2 \mid n \rangle = \langle n \mid p^2/2m \mid n \rangle \tag{142}$$

implying that the expectation values of the potential and kinetic energies are equal.

PROBLEM 8.8

Prove

$$a\bar{a}^n - \bar{a}^n a = n\bar{a}^{n-1} \tag{143}$$

(*Hint*: Multiply by $\bar{a}$ on the left and prove by induction).

PROBLEM 8.9

Consider the operator

$$N_{op} = \bar{a}a \tag{144}$$

Show that it commutes with the Hamiltonian and that its eigenvalues are 0, 1, 2, . . . For this reason N_{op} is called the number operator.

PROBLEM 8.10

If an operator P contains p creation operators $\bar{a}$ and q annihilation operators a (arranged in any order) then show that $\langle n \mid P \mid n \rangle$ is zero unless $p = q$.

PROBLEM 8.11

Show that the operator $\bar{a}$ cannot have any eigenkets and similarly a cannot have any eigenbras.

PROBLEM 8.12

We refer to the spherical harmonics discussed in Sec. 6.4.

(*a*) Show that Y_{00} is a simultaneous eigenfunction of L^2, L_x, L_y and L_z. What are the corresponding eigenvalues?

(*b*) Show that $Y_{1,1}$, $Y_{1,0}$ and $Y_{1,-1}$ are simultaneous eigenfunctions of L^2 and L_z but are not eigenfunctions of L_x and L_y. Construct appropriate linear combinations which are simultaneous eigenfunctions of L^2 and L_x and also of L^2 and L_y. (*Hint*: Use Eqs. (30) and (31) of Chapter 9 and the fact that $L_x = \frac{1}{2}(L_+ + L_-)$ etc.)

(*c*) Similarly construct appropriate linear combinations for the $l = 2$ case.

PROBLEM 8.13

Consider the angular momentum matrices for $j = \frac{1}{2}$ (see Eq. 35 of Chapter 9). Show that the kets $\mid 1 \rangle$ and $\mid 2 \rangle$ defined through Eqs. (40) and (41) (of Chapter 9) are simultaneous eigenkets of J^2 and J_z but are not eigenkets of J_x and J_y; however, the kets $\mid \hat{x} \uparrow \rangle$ and $\mid \hat{x} \downarrow \rangle$ [defined through Eqs. (42) and (43) of Chapter 9] are simultaneous eigenkets of J^2 and J_x but not of J_y and J_z.

PROBLEM 8.14

Prove that the operators

$$p_{op} = -i\hbar\,\frac{\partial}{\partial x} \quad \text{and} \quad H = -\,\frac{\hbar^2}{2m}\,\frac{d^2}{dx^2} + V(x)$$

are real operators.

PROBLEM 8.15

Show that the operator xp_x is not real but $\frac{1}{2}(xp_x + p_x x)$ is a real operator.

PROBLEM 8.16

Prove that the operator $-i\hbar\,\partial/\partial r$ is not real but the operator

$$p_r = -\,i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \tag{145}$$

is a real operator.

PROBLEM 8.17

Prove that

$$(a) \quad \langle x \mid p_{op} \mid p\rangle = -i\hbar\,\frac{d}{dx}\langle x \mid p\rangle \tag{146}$$

$$(b) \quad \langle x \mid p_{op} \mid \Psi\rangle = -i\hbar\,\frac{d}{dx}\langle x \mid \Psi\rangle \tag{147}$$

PROBLEM 8.18

Generalize the formulae in Sec. 8.8 to three dimensions; in particular, prove that

$$\int d\mathbf{r} \mid \mathbf{r}\rangle\langle \mathbf{r} \mid = 1 = \int d\mathbf{p} \mid \mathbf{p}\rangle\langle \mathbf{p} \mid \tag{148}$$

$$\langle \mathbf{r} \mid \mathbf{r}'\rangle = \delta(\mathbf{r} - \mathbf{r}') \tag{149}$$

$$\langle \mathbf{r} \mid \mathbf{p}_{op} \mid \mathbf{p}\rangle = -i\hbar\,\nabla\langle \mathbf{r} \mid \mathbf{p}\rangle \tag{150}$$

$$\langle \mathbf{r} \mid \mathbf{p}_{op} \mid \Psi\rangle = -i\hbar\,\nabla\langle \mathbf{r} \mid \Psi\rangle \tag{151}$$

PROBLEM 8.19

Show that the coherent states satisfy the following equations

$$(a) \quad \mid\langle n \mid \alpha\rangle\mid^2 = \frac{1}{n!}\left(\mid\alpha\mid^2\right)^n \exp\left[-\,\frac{1}{2}\mid\alpha\mid^2\right] \tag{152}$$

(b) If $\mid\beta\rangle$ is another eigenket of a, then

$$\mid\langle\alpha \mid \beta\rangle\mid^2 = \exp\left[-\mid\alpha - \beta\mid^2\right] \tag{153}$$

(Notice that the eigenkets are not orthogonal; why?)

$$(c)\quad \Delta x\,\Delta p = \frac{1}{2}\hbar \tag{145}$$

$$(d)\quad \langle x \mid \alpha \rangle = N \exp\left[-\frac{\omega}{2\hbar}x^2 + \left(\frac{2\omega}{\hbar}\right)^{1/2}\alpha x\right] \tag{155}$$

The above equation tells us that $\langle x \mid \alpha \rangle$ is a Gaussian (with maximum value at $x = \alpha(2\hbar/\omega)^{1/2}$) and hence the uncertainty product is always $1/2\hbar$.

Problem 8.20

Prove that

$$[a, e^{\alpha\bar{a}}] = \alpha\, e^{\alpha\bar{a}} \tag{156}$$

where α is an arbitrary complex number. Using the above equation show that $\exp(\alpha\bar{a}) \mid 0\rangle$ is an eigenket of the operator a. What is the corresponding eigenvalue?

(*Hint*: Expand the exponential and use Eq. (143). In the second part of the problem operate Eq. (156) on $\mid 0\rangle$).

Problem 8.21

Let a dynamical system be in an eigenstate $\mid n\rangle$ of the Hamiltonian. If a measurement of an observable α is made then show that the probability of obtaining the eigenvalue α_m is

$$\mid \langle \alpha_m \mid n \rangle \mid^2.$$

Problem 8.22

Let us define the real operators J_x, J_y and J_z through the following equations

$$J_x = \tfrac{1}{2}[\bar{a}_2 a_1 + \bar{a}_1 a_2] \tag{157}$$

$$J_y = \tfrac{1}{2}\, i[\bar{a}_2 a_1 - \bar{a}_1 a_2] \tag{158}$$

and

$$J_z = \tfrac{1}{2}[\bar{a}_1 a_1 - \bar{a}_2 a_2] \tag{159}$$

Assuming

$$[a_1, a_2] = [\bar{a}_1, \bar{a}_2] = 0 \tag{160}$$

and

$$[a_i, \bar{a}_k] = \delta_{ik};\ i, k = 1, 2 \tag{161}$$

show that

$$[J_z, J_\pm] = \pm J_\pm \text{ and } [J_+, J_-] = 2J_z \tag{162}$$

where

$$J_+ = J_x + iJ_y = \bar{a}_1 a_2 \tag{163}$$

and

$$J_- = J_x - iJ_y = \bar{a}_2 a_1 \tag{164}$$

Thus J_x, J_y and J_z satisfy the same commutation relations as the components of the angular momentum operator. Notice that a_1, $\bar{a}_1$ and a_2, $\bar{a}_2$ represent the pairs of the annihilation and creation operators for a two dimensional isotropic harmonic oscillator (see Problem 8.24).

PROBLEM 8.23

Using the results of the previous problem prove that

$$J^2 = \alpha(\alpha + 1) \tag{165}$$

where

$$\alpha = \tfrac{1}{2}(\bar{a}_1 a_1 + \bar{a}_2 a_2) \tag{166}$$

Thus the eigenfunctions of the number operators are eigenvalues of J^2 (the converse is not true).

Hint : First show that

$$J^2 = \tfrac{1}{2}(J_+J_- + J_-J_+) + J_z^2$$

PROBLEM 8.24

(*a*) Show that the Hamiltonian for a two dimensional isotropic oscillator can be written in the form

$$H = (a_1\bar{a}_1 + a_2\bar{a}_2 + 1)\,\hbar\omega \tag{167}$$

where

$$a_1 = \frac{1}{\sqrt{2m\hbar\omega}}\left(m\omega x + ip_x\right) \tag{168}$$

and

$$a_2 = \frac{1}{\sqrt{2m\hbar\omega}}\left(m\omega y - ip_y\right) \tag{169}$$

Show that the eigenvalues would be $\hbar\omega$, $2\hbar\omega$, . . . and the eigenvalue $n\hbar\omega$ will be n-fold degenerate.

(*b*) Show that the angular momentum operator L defined as

$$L = \frac{1}{\hbar}\left(xp_y - yp_x\right) = i\left(a_1\bar{a}_2 - \bar{a}_1 a_2\right) \tag{170}$$

is a constant of motion.

(*c*) If $\alpha_1 \equiv \frac{1}{\sqrt{2}}\left(a_1 - ia_2\right)$

and

$$\alpha_2 \equiv \frac{1}{\sqrt{2}}\left(a_1 + ia_2\right) \tag{171}$$

prove that

$$\left.\begin{array}{l}[\alpha_i, \alpha_j] = [\bar{\alpha}_i, \bar{\alpha}_j] = 0 \\ \text{and} \\ [\alpha_i, \bar{\alpha}_j] = \delta_{ij}\end{array}\right\} i, j = 1, 2 \tag{172}$$

Hence show that the eigenvalues of the operators

$$N_1 = \bar{\alpha}_1 \alpha_1 \quad \text{and } N_2 = \bar{\alpha}_2 \alpha_2 \tag{173}$$

are 0, 1, 2, . . .

(*d*) If $| n_1, n_2 \rangle$ represents a simultaneous eigenket of N_1 and N_2, then show that it is also an eigenket of H and L.

PROBLEM 8.25

Prove that

$$e^{\lambda A} B e^{-\lambda A} = B + \lambda[A, B] + \frac{\lambda^2}{2!}\Big[A, [A, B]\Big] + \frac{\lambda^3}{3!}\Big[A, [A, [A, B]]\Big] + \cdots \tag{174}$$

(*Hint* : Expand the exponential.)

PROBLEM 8.26

Prove that

$$e^{A+B} = e^A e^B e^{-1/2[A,B]} \tag{175}$$

if

$$[A, [A, B]] = [B, [A, B]] = 0 \tag{176}$$

PROBLEM 8.27

(*a*) Consider two operators b and $\bar{b}$ which satisfy the following anticommutation relations*

$$\{b, b\}_+ = 0, \quad \{\bar{b}, \bar{b}\}_+ = 0 \tag{177}$$

and

$$\{b, \bar{b}\}_+ = 1 \tag{178}$$

where

$$\{\alpha, \beta\}_+ = \alpha\beta + \beta\alpha \tag{179}$$

Prove that the eigenvalues of the number operator N $(= \bar{b}\, b)$ are 1 and 0.

(*b*) Show that the operators $\bar{b}$ and b act as creation and annihilation operators.

---

*The operators b and $\bar{b}$ are known as Fermion annihilation and creation operators.

PROBLEM 8.28

Assuming

$$\rho = (1 - e^{-\xi})\, e^{-\xi \bar{a} a}$$

[see Eq. (125)]

show that

(i) $\text{Tr}\, \rho = 1$, and

(ii) $\langle n \rangle = (e^{\xi} - 1)^{-1}$

[*Hints* : $\langle n \rangle = \langle \bar{a} a \rangle = \text{Tr}\, (\bar{a} a \rho)$]

PROBLBM 8.29

The density operator

$$\rho = \frac{1}{Z} \exp[-\beta H], \; \beta = \frac{1}{kT} \tag{180}$$

describes an ensemble of harmonic oscillators in thermodynamic equilibrium at temperature T; here

$$Z = \text{Tr}\, [\exp(-\beta H)] \tag{181}$$

is known as the partition function. Show that

$$\langle E \rangle = \text{Tr}\, (\rho H) = -\frac{\partial}{\partial \beta} \ln Z \tag{182}$$

and the entropy is given by

$$S = -k\, \text{Tr}\, (\rho \ln \rho) = k[\ln Z + \beta \langle E \rangle] \tag{183}$$

PROBLEM 8.30

Show for a pure state

$$\rho^2 = \rho \tag{184}$$

PROBLEM 8.31

Consider a two state system like the two spin states of an electron. Consider the state

$$c_1 \,|\, \mathbf{z} \uparrow \rangle + c_2 \,|\, \mathbf{z} \downarrow \rangle$$

where $|\, \mathbf{z} \uparrow \rangle$ and $|\, \mathbf{z} \downarrow \rangle$ represent the states in which the z-component of the spin angular momentum is pointing upwards and downwards respectively (see Chapter 5). Representing the $|\, \mathbf{z} \uparrow \rangle$ and $|\, \mathbf{z} \downarrow \rangle$ by

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

show that the density operator of the state

$$c_1 \mid z\uparrow\rangle + c_2 \mid z\downarrow\rangle$$

is given by

$$\begin{pmatrix} |c_1|^2 & c_1c_2^* \\ c_2c_1^* & |c_2|^2 \end{pmatrix}$$

SOLUTIONS

SOLUTION 8.1

The identity (see Appendix *F*)

$$\int \delta(x-x')\,\delta(x-x'')\,dx = \delta(x'-x'') \tag{185}$$

shows that orthonormality of wavefunctions [cf. Eq. (42)], notice that the Kronecker delta function [see Eq. (31)] is replaced by a Dirac delta function. The equation

$$f(x) = \int_{-\infty}^{+\infty} f(x')\,\delta(x-x')\,dx' \tag{186}$$

tells us that an arbitrary function can be expanded in terms of the eigenfunctions of the operator x.

SOLUTION 8.2

The solution of Eq. (137) is

$$\psi_p(x) = \frac{1}{(2\pi\hbar)^{1/2}}\exp\left[\frac{i}{\hbar}px\right] \tag{187}$$

where the factor $(2\pi\hbar)^{-1/2}$ is such that

$$\int_{-\infty}^{+\infty} \psi_p^*(x)\,\psi_{p'}(x)\,dx = \delta(p-p') \tag{188}$$

which is the orthonormality condition; notice once again the Dirac delta function which always appears for continuum eigenfunctions. Obviously p in Eq. (187) is just a number and it can have any real value between $-\infty$ and $+\infty$; a complex value of p will make ψ_p diverge at $x \to +\infty$ or $-\infty$. The Fourier transform equation

$$f(x) = \int_{-\infty}^{+\infty} a(p)\left[\frac{1}{\sqrt{2\pi\hbar}}\exp\left(\frac{i}{\hbar}px\right)\right]dp$$

suggests that an arbitrary function can be expanded in terms of $\psi_p(x)$. Alternatively the equation (see Appendix D)

$$\int \psi_p^*(x')\, \psi_p(x)\, dp = \delta(x - x') \tag{189}$$

gives the completeness condition [cf. Eqs. (37) and (47)]. Notice that $\psi_p(x)$ is an eigenfunction of the free particle Hamiltonian $[= -(\hbar^2/2m)\,(d^2/dx^2)]$.

SOLUTION 8.5

Let $\alpha = |\,P\rangle\langle Q\,|$ and $|\,B\rangle = \alpha\,|\,A\rangle = |\,P\rangle[\langle Q\,|\,A\rangle]$

then

$$\langle B\,| = \langle A\,|\,\bar{\alpha} = \langle P\,|\,\overline{\langle Q\,|\,A\rangle} = \langle A\,|\,Q\rangle\langle P\,|$$

Thus

$$\bar{\alpha} = |\,Q\rangle\langle P\,|$$

SOLUTION 8.7

Using Eqs. (67), (68) and (71), we get

$$\begin{aligned}\langle m\,|\,x\,|\,n\rangle &= \left(\frac{\hbar}{2m\omega}\right)^{1/2} \langle m\,|\,\bar{a} + a\,|\,n\rangle \\ &= \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left[\sqrt{n+1}\,\langle m\,|\,n+1\rangle + \sqrt{n}\, m\langle\,|\,n-1\rangle\right] \\ &= \left(\frac{\hbar}{2m\omega}\right)^{1/2}\left[\sqrt{n+1}\,\delta_{m,n+1} + \sqrt{n}\,\delta_{m,n-1}\right] \qquad (190)\end{aligned}$$

Similarly

$$\langle m\,|\,p\,|\,n\rangle = i\left(\frac{m\hbar\omega}{2}\right)^{1/2}\left[\sqrt{n+1}\,\delta_{m,n+1} - \sqrt{n}\,\delta_{m,n-1}\right] \tag{191}$$

and

$$\langle m\,|\,H\,|\,n\rangle = \left(n + \frac{1}{2}\right)\hbar\omega\,\delta_{m,n}$$

Thus the matrices which represent x and p are

$$x = \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} \begin{bmatrix} 0 & \sqrt{1} & 0 & 0 & . & . & . \\ \sqrt{1} & 0 & \sqrt{2} & 0 & . & . & . \\ 0 & \sqrt{2} & 0 & \sqrt{3} & . & . & . \\ 0 & 0 & \sqrt{3} & 0 & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \end{bmatrix} \tag{192}$$

$$p = \left(\frac{m\hbar\omega}{2}\right)^{\frac{1}{2}} \begin{bmatrix} 0 & -i\sqrt{1} & 0 & 0 & . & . & . \\ i\sqrt{1} & 0 & -i\sqrt{2} & 0 & . & . & . \\ 0 & i\sqrt{2} & 0 & -i\sqrt{3} & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \end{bmatrix} \tag{193}$$

and H is a diagonal matrix with diagonal elements $\frac{1}{2}\hbar\omega$, $\frac{3}{2}\hbar\omega$, . . . Notice that all matrices are Hermitian.

SOLUTION 8.12

(*b*) Using Eqs. (30) and (31) of Chapter 9, we get

$$L_x\, Y_{1,1} = \frac{1}{2}\,(L_+ + L_-)\mid 1, 1\rangle = \frac{1}{\sqrt{2}}\, Y_{1,0}$$

$$L_x\, Y_{1,0} = \frac{1}{\sqrt{2}}(Y_{1,1} + Y_{1,-1})$$

$$L_x\, Y_{1,-1} = \frac{1}{\sqrt{2}}\, Y_{1,0}$$

Simple manipulations show that $(Y_{1,1} - Y_{1,-1})$, $(Y_{1,1} + Y_{1,-1} + \sqrt{2}\, Y_{1,0})$ and $(Y_{1,1} + Y_{1,-1} - \sqrt{2}\, Y_{1,0})$ are eigenfunctions of L_x.

SOLUTION 8.14

In order to prove that the operator p_x is real we must show [see Eqs. (18) (26) and (38)]

$$\int_{-\infty}^{+\infty} \varphi^* p_x \psi\, dx = \left[\int_{-\infty}^{+\infty} \psi^* p_x\, \varphi\, dx\right]^* \tag{194}$$

Now

$$\left[\int_{-\infty}^{+\infty} \psi^* p_x\, \varphi\, dx\right]^* = \left[-i\hbar \int_{-\infty}^{+\infty} \psi^* \frac{d\varphi}{dx}\right]^* = i\hbar \int_{-\infty}^{+\infty} \psi\, \frac{d\varphi^*}{dx}\, dx$$

$$= i\hbar\left[\psi\varphi^* \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \varphi^* \frac{d\psi}{dx}\, dx\right] = \int_{-\infty}^{+\infty} \varphi^* p_x \psi\, dx$$

proving Eq. (194); in obtaining the last step we have assumed the wavefunctions vanish at $\pm\,\infty$.

SOLUTION 8.16

It is necessary to show that

$$\int_0^\infty \varphi^* p_r \psi r^2 dr = \left[\int_0^\infty \psi^* p_r \varphi r^2 dr\right]^* \tag{195}$$

which can be proved by carrying out integration by parts, etc.

SOLUTION 8.17

(*a*) $\langle x \mid p_{op} \mid p \rangle = p \langle x \mid p \rangle$ [Using Eq. (43); p is just a number]

$$= p \frac{1}{\sqrt{2\pi\hbar}} \exp(ipx/\hbar) \quad \text{[Using Eq. (44)]}$$

$$= -i\hbar \frac{d}{dx} \langle x \mid p \rangle \tag{196}$$

(*b*) $\langle x \mid p_{op} \mid \Psi \rangle = \langle x \mid p_{op} \int dp \mid p \rangle \langle p \mid \Psi \rangle$ [Using Eq. (47)]

$$= -i\hbar \frac{d}{dx} \int dp \langle x \mid p \rangle \langle p \mid \Psi \rangle \quad \text{[Using Eq. (196)]}$$

$$= -i\hbar \frac{d}{dx} \langle x \mid \Psi \rangle \quad \text{[Using Eq. (47)]}$$

SOLUTION 8.19

$$(d) \quad a \mid \alpha \rangle = \frac{m\omega x + ip}{\sqrt{2m\hbar\omega}} \mid \alpha \rangle = \alpha \mid \alpha \rangle \tag{197}$$

Thus

$$m\omega x \langle x \mid \alpha \rangle + \hbar \frac{d}{dx} \langle x \mid \alpha \rangle = \sqrt{2m\hbar\omega}\, \alpha \langle x \mid \alpha \rangle \text{ etc.}$$

SOLUTION 8.26

Let $F(\lambda) = e^{\lambda A} e^{\lambda B}$, then

$$\frac{dF}{d\lambda} = [A + e^{\lambda A} B e^{-\lambda A}] F(\lambda)$$

$$= (A + B) F(\lambda) + \lambda [A, B] F(\lambda)$$

where we have used Eq. (174). Since $(A + B)$ commutes with (A, B), the solution is

$$F(\lambda) = e^{(A+B)\lambda} e^{1/2 [A, B] \lambda^2} \tag{198}$$

where we have used the condition $F(0) = 1$. Putting $\lambda = 0$ gives Eq. (175).

SOLUTION 8.27

Equations (177) and (178) give us

$$b^2 = 0 = \bar{b}^2 \quad \text{and} \quad \bar{b}b + \bar{b}b = 1$$

Thus

$$N^2 = \bar{b}b\bar{b}b = \bar{b}(1 - \bar{b}b)\, b = \bar{b}b = N \tag{199}$$

From the eigenvalue equation

$$N \mid n\rangle = n \mid n\rangle$$

we get

$$N^2 \mid n\rangle = nN \mid n\rangle = n^2 \mid n\rangle$$

since $N^2 = N$, $n^2 = n$ giving $n = 0, 1$ consistent with the Pauli's exclusion principle. Since $Nb = bN - b$ we have

$$0 = N\{b \mid n\rangle\} = \{bN - b\} \mid n\rangle = (n - 1)\{b \mid n\rangle\}$$

Thus $b \mid n\rangle$ is an eigenket of N belonging to the eigenvalue $(n - 1)$. Obviously

$$b \mid 1\rangle = \mid 0\rangle \quad \text{and} \quad b \mid 0\rangle = 0 \text{ (null ket)} \tag{200}$$

Similarly

$$\bar{b} \mid 0\rangle = \mid 1\rangle \qquad \text{and} \qquad \bar{b} \mid 1\rangle = 0 \tag{201}$$

CHAPTER 9

Angular Momentum II

9.1 Introduction

In Chapter 6 we had introduced the quantum mechanical angular momentum operator **L** and had shown that its components satisfy the following commutation relations

$$\left.\begin{aligned}[L_x, L_y] &= i\hbar\, L_z\\ [L_y, L_z] &= i\hbar\, L_x\\ [L_z, L_x] &= i\hbar\, L_y\end{aligned}\right\} \tag{1}$$

We had also shown that the square of the angular momentum operator $L^2(\equiv L_x^2 + L_y^2 + L_z^2)$ commutes with L_x, L_y and L_z; i.e.,

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0 \tag{2}$$

In this chapter we will use just these commutation relations and will show that if one makes a measurement of a Cartesian component of the angular momentum operator then it will always be an integral or a half integral multiple of $\hbar$, a result which is one of the remarkable features of quantum mechanics. It may be mentioned that in Chapter 6 we had shown that L_z (and similarly L_x and L_y) can only have eigenvalues 0, $\hbar$, $2\hbar$, . . . etc.

In Sec. 9.2 we will discuss the eigenvalue spectrum of a Cartesian component of the angular momentum operator and of the square of the angular momentum operator. In Sec. 9.3 we will consider the representation of the angular momentum operator in terms of matrices and discuss their significance. In Sec. 9.4 we will discuss the famous Stern-Gerlach experiment which demonstrated the quantization of angular momentum. In Sec. 9.5 we will discuss the wavefunction describing an electron taking into account its spin angular momentum. In Sec. 9.6 we will show how a spinor transforms under rotation which will enable us to have a better understanding of the Stern-Gerlach experiment.

9.2 Eigenvalues

In this section we will use the commutation relations [see Eqs. (1) and (2)] to deduce the eigenvalues of a particular component of the angular momentum operator. For reasons to be discussed later, we will denote the angular momentum operator by **J** and use a system of units in which $\hbar = 1$. Thus, Eqs. (1) and (2) become

$$[J_x, J_y] = iJ_z \tag{3}$$

$$[J^2, J_z] = 0 \tag{4}$$

and other equations can be written in cyclic order.

It is convenient to use the Dirac notation introduced in the previous chapter. Since, J^2 and J_z commute, we can construct a complete set of orthonormal eigenkets which are simultaneous eigenkets $|\,\lambda, m\rangle$ of the operators J^2 and J_z belonging to the eigenvalues λ and m respectively (see Sec. 8.10). Thus,

$$J^2\,|\,\lambda, m\rangle = \lambda\,|\,\lambda, m\rangle \tag{5}$$

$$J_z\,|\,\lambda, m\rangle = m\,|\,\lambda, m\rangle \tag{6}$$

We define the so called *ladder operators*

$$J_+ = J_x + i J_y \tag{7}$$

and $$J_- = J_x - i J_y \tag{8}$$

Now $$\begin{aligned}[J_z, J_+] &= [J_z, J_x] + i[J_z, J_y] \\ &= i J_y + J_x = J_+\end{aligned}$$

Thus $$[J_z, J_+] = J_+ \tag{9}$$

Similarly $$[J_z, J_-] = -J_- \tag{10}$$

We also have $J_+J_- = J_x^2 + J_y^2 - i[J_x, J_y]$

or $$J_+J_- = J^2 - J_z^2 + J_z \tag{11}$$

Similarly $$J_-J_+ = J^2 - J_z^2 - J_z \tag{12}$$

Further, $$\overline{J}_+ = J_- \tag{13}$$

and $$\overline{J}_- = J_+ \tag{14}$$

i.e., J_- and J_+ are adjoints of J_+ and J_- respectively.

We first show that $\lambda \geqslant m^2$. Now

$$\begin{aligned}\langle P\,|\,J^2 - J_z^2\,|\,P\rangle = \langle P\,|\,J_x^2 + J_y^2\,|\,P\rangle &= \langle P\,|\,J_xJ_x\,|\,P\rangle \\ &\quad + \langle P\,|\,J_yJ_y\,|\,P\rangle \\ &= \langle Q\,|\,Q\rangle + \langle R\,|\,R\rangle \geqslant 0\end{aligned} \tag{15}$$

where $|\,Q\rangle = J_x\,|\,P\rangle$, $|\,R\rangle = J_y\,|\,P\rangle$ and since J_x and J_y are observables (and hence Hermitian) $\langle Q\,| = \langle P\,|\,\overline{J}_x = \langle P\,|\,J_x$ and $\langle R\,| = \langle P\,|\,J_y$. In the last step of Eq. (15) we have used Eq. (6) of Chapter 8. If we choose $|\,P\rangle = |\,\lambda, m\rangle$ then

$$0 \leqslant \langle\lambda, m\,|\,J^2 - J_z^2\,|\,\lambda, m\rangle = (\lambda - m^2)\,\langle\lambda, m\,|\,\lambda, m\rangle$$

Thus

$$\lambda \geqslant m^2 \tag{16}$$

We next consider the effect of the ladder operator on the ket $|\,\lambda, m\rangle$. Using Eq. (9) we get

$$J_zJ_+\,|\,\lambda, m\rangle = (J_+ + J_+J_z)\,|\,\lambda, m\rangle$$

or $$J_z(J_+\,|\,\lambda, m\rangle) = (m+1)\,(J_+\,|\,\lambda, m\rangle) \tag{17}$$

Further, since J^2 commutes with J_x and J_y we will have

$$[J^2, J_\pm] = 0$$

or $$J^2 J_\pm |\lambda, m\rangle = J_\pm J^2 |\lambda, m\rangle$$

or $$J^2 (J_\pm |\lambda, m\rangle) = \lambda (J_\pm |\lambda, m\rangle) \tag{18}$$

Equations (17) and (18) tell us that $J_+ |\lambda, m\rangle$ is a simultaneous eigenket of the operators J^2 and J_z belonging to the eigenvalues λ and $(m + 1)$, provided $J_+ |\lambda, m\rangle$ is not a null ket. Similarly, using Eq. (10) we can show that

$$J_z[J_- |\lambda, m\rangle] = (m - 1)\,[J_- |\lambda, m\rangle] \tag{19}$$

implying that $J_- |\lambda, m\rangle$ is a simultaneous eigenket of J^2 and J_z belonging to the eigenvalues λ and $(m - 1)$ respectively provided it is not a null ket. We may, therefore, write

$$J_+ |\lambda, m\rangle = C_+ |\lambda, m + 1\rangle \tag{20}$$

and

$$J_- |\lambda, m\rangle = C_- |\lambda, m - 1\rangle \tag{21}$$

These equations show why J_+ and J_- are called *ladder* operators. J_+ is an operator that 'raises' the eigenket to the next higher value of m and similarly J_- is a 'lowering' operator. In a similar manner we may argue to show that $J_+ |\lambda, m + 1\rangle$ and $J_- |\lambda, m - 1\rangle$ are proportional to $|\lambda, m + 2\rangle$ and $|\lambda, m - 2\rangle$ respectively. This, however, cannot go on indefinitely; otherwise we will violate the condition $\lambda \geqslant m^2$. Consequently, there must exist a particular value of m, say $m = j$, for which

$$J_+ |\lambda, j\rangle = 0 \tag{22}$$

Operating on the left by J_-, we obtain [using Eq. (12)]

$$(J^2 - J_z^2 - J_z) |\lambda, j\rangle = 0$$

or

$$(\lambda - j^2 - j) |\lambda, j\rangle = 0 \tag{23}$$

Since, $|\lambda, j\rangle \neq 0$, the number $\lambda - j^2 - j = 0$; and hence*,

$$\lambda = j(j + 1) \tag{24}$$

We can determine the lowest value of m, say j' by requiring

$$J_- |\lambda, j'\rangle = 0$$

---

*The reader not yet attuned to operator algebra may pause here and reflect on Eqs. (22) and (23) to see how we treat them differently. In Eq. (22) neither the operator J_+ nor the ket $|\lambda, j\rangle$ need be zero in order to produce a null ket. For example, $d^2(x)/dx^2 = 0$ does not permit us to identify either d^2/dx^2 or x with a null quantity. But in Eq. (23), a ket is multiplied by a number and one of them must vanish.

Operating on the left by $\mathcal{J}_+$ and using Eq. (11) we obtain

$$(\lambda - j'^2 + j') = 0$$

or $$\lambda = j'(j' - 1) \tag{25}$$

Using Eqs. (24) and (25) we obtain $j' = j + 1$ (which we reject since j' is supposed to be less than j), or

$$j' = -j \tag{26}$$

Thus, we have a family of kets which correspond to the same eigenvalue $\lambda\,[= j(j+1)]$ of $\mathcal{J}^2$ but different eigenvalues of $\mathcal{J}_z$. These we denote by

$$|\lambda, j\rangle, |\lambda, j-1\rangle, \ldots, |\lambda, -j\rangle \tag{27}$$

Successive applications of the ladder operator $\mathcal{J}_-$ on $|\lambda, j\rangle$ should ultimately lead to* $|\lambda, -j\rangle$. This will only happen if $2j$ is an integer, so that the allowed values of j are

$$j = 0, 1/2, 1, 3/2, \ldots, \text{etc.} \tag{28}$$

and for each value of j the m values go from $-j$ to j in steps of unity. Thus there are $(2j+1)$ eigenkets of $\mathcal{J}^2$, each having the same eigenvalue $j(j+1)$. We label the eigenkets as

$$|j, m\rangle;\ m = -j, -j+1, \ldots, j-1, j$$

with $j = 0, 1/2, 1, 3/2 \ldots$ The kets stisfy the orthonormality condition

$$\langle j', m' | j, m\rangle = \delta_{jj'}\,\delta_{mm'} \tag{29}$$

Thus, from the commutation rules of angular momenta, it appears that angular momentum components (say $\mathcal{J}_z$) can have half integral values. On the other hand, components of orbital angular momenta, defined as $\mathbf{r}\times\mathbf{p}$, can have only eigenvalues 0, $\hbar$, $2\hbar$, etc. (see Sec. 6.3). The question arises whether nature provides systems which do have $\frac{1}{2}\hbar$ values for angular momenta. It is remarkable that the most elementary system known, the electron, is an example of this. Obviously we cannot write this spin angular momentum as an operator operating on the co-ordinates of the electron. Spin has no classical analogue and is introduced in non-relativistic theory *ad hoc.* We shall see that the Dirac theory (Chapter 23) provides a natural explanation of this. The suggestion about spin came from a study of Zeeman patterns from which it appeared that the $(2l+1)$ multiplicity of levels often turned out to be even. (see Fig. 21.4).

In a closed complex system such as an atom one can only talk of a total angular momentum. One may think that, in principle, it would be possible to construct this total angular momentum from the pieces of the atom by considering the details of internal dynamics. Even this is incorrect unless a spin assignment is made to the elementary particles, the pieces of the atom. An attempt, in fact, was made to attribute spin to the rotation of the electron about its axis but this exercise proved abortive*.

---

*Also, successive applications of $\mathcal{J}_+$ on $|\lambda, -j\rangle$ should lead to $|\lambda, j\rangle$.

9.2.1 THE CONSTANTS C_+ AND C_-

We now determine the normalization constants C_+ and C_- in Eqs. (20) and (21). First, we note that if we define

$$|P\rangle = J_+|j, m\rangle = C_+|j, m+1\rangle$$

then $\langle P| = \langle j, m|J_- = C_+^*\langle j, m+1|$ (since $\overline{J}_+ = J_-$)

Thus $\langle P|P\rangle = \langle j, m|J_-J_+|j, m\rangle = |C_+|^2\langle j, m+1|j, m+1\rangle$

But

$$\langle j, m|J_-J_+|j, m\rangle = \langle j, m|J^2 - J_z^2 - J_z|j, m\rangle$$
$$= j(j+1) - m^2 - m = (j-m)(j+m+1)$$

Hence

$$C_+ = [(j-m)(j+m+1)]^{1/2}$$

or

$$J_+|j, m\rangle = [(j-m)(j+m+1)]^{1/2}|j, m+1\rangle \tag{30}$$

Similarly $J_-|j, m\rangle = [(j+m)(j-m+1)]^{1/2}|j, m-1\rangle$ (31)

Notice that the coefficients in front of $|j, m+1\rangle$ and $|j, m-1\rangle$ are zero for $m = +j$ and $m = -j$ respectively. Thus

$$J_+|j, j\rangle = 0$$

and $J_-|j, -j\rangle = 0$

9.3 Angular Momentum Matrices Corresponding to $j = \frac{1}{2}$ and the Pauli Spin Matrices

We will consider the matrix representation of the components of the angular momentum operator (corresponding to $j = \frac{1}{2}$) in a system in which J^2 and J_z are diagonal, i.e., we will choose as basis vectors the simultaneous eigenfunctions of J^2 and J_z. Now, corresponding to $j = \frac{1}{2}$ we have $m = \frac{1}{2}$ and $-\frac{1}{2}$, thus we have two base states which we denote by $|1\rangle$ and $|2\rangle$.

$$|1\rangle = |\tfrac{1}{2}, \tfrac{1}{2}\rangle = |j = \tfrac{1}{2}, m = \tfrac{1}{2}\rangle \tag{32}$$

and

$$|2\rangle = |\tfrac{1}{2}, -\tfrac{1}{2}\rangle = |j = \tfrac{1}{2}, m = -\tfrac{1}{2}\rangle \tag{33}$$

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*As long as one considers a complex system such as the nucleus, as a whole, one can only talk of its intrinsic total angular momentum. This is often loosely referred to as 'spin' but strictly, there is no such thing.

obviously

$$\left.\begin{aligned} \mathcal{J}_z|1\rangle &= \tfrac{1}{2}\hbar|1\rangle, \quad \mathcal{J}_z|2\rangle = -\tfrac{1}{2}\hbar|2\rangle \\ \mathcal{J}^2|1\rangle &= \tfrac{3}{4}\hbar^2|1\rangle, \quad \mathcal{J}^2|2\rangle = \tfrac{3}{4}\hbar^2|2\rangle \end{aligned}\right\} \tag{34}$$

The (ij)th matrix element of an operator $\mathcal{O}$ is defined by

$$\mathcal{O}_{ij} = \langle i|\mathcal{O}|j\rangle$$

Consequently

$$(\mathcal{J}_z)_{12} = \langle 1|\mathcal{J}_z|2\rangle = 0 = \langle 2|\mathcal{J}_z|1\rangle = (\mathcal{J}_z)_{21}$$

$$(\mathcal{J}_z)_{11} = \langle 1|\mathcal{J}_z|1\rangle = \tfrac{1}{2}\hbar, \; (\mathcal{J}_z)_{22} = \langle 2|\mathcal{J}_z|2\rangle = -\tfrac{1}{2}\hbar$$

Similarly $(\mathcal{J}^2)_{12} = (\mathcal{J}^2)_{21} = 0$

and $\quad (\mathcal{J}^2)_{11} = (\mathcal{J}^2)_{22} = \tfrac{3}{4}\hbar^2$

Now

$$\begin{aligned} \langle j, m'|\mathcal{J}_x|j, m\rangle &= \langle j, m'|\tfrac{1}{2}[\mathcal{J}_+ + \mathcal{J}_-]|j, m\rangle \\ &= \tfrac{1}{2}[(j+m+1)(j+m)]^{1/2}\hbar\,\langle j, m'|j, m+1\rangle \\ &\quad + \tfrac{1}{2}[(j+m)(j-m+1)]^{1/2}\hbar\,\langle j, m'|j, m-1\rangle \\ &= \tfrac{1}{2}[(j+m+1)(j-m)]^{1/2}\hbar\,\delta_{m', m+1} \\ &\quad + \tfrac{1}{2}[(j+m)(j-m+1)]^{1/2}\hbar\,\delta_{m', m-1} \end{aligned}$$

i.e., the matrix element is zero unless $m' = m + 1$ or $m - 1$. Thus

$$(\mathcal{J}_x)_{11} = \langle 1|\mathcal{J}_x|1\rangle = \langle \tfrac{1}{2}, \tfrac{1}{2}|\mathcal{J}_x|\tfrac{1}{2}, \tfrac{1}{2}\rangle = 0$$

and similarly $(\mathcal{J}_x)_{22} = 0$. However,

$$\begin{aligned} (\mathcal{J}_x)_{12} &= \langle 1|\mathcal{J}_x|2\rangle = \langle \tfrac{1}{2}, \tfrac{1}{2}|\mathcal{J}_x|\tfrac{1}{2}, -\tfrac{1}{2}\rangle \\ &= \tfrac{1}{2}[(\tfrac{1}{2} - \tfrac{1}{2} + 1)(\tfrac{1}{2} + \tfrac{1}{2})]^{1/2}\,\hbar = \tfrac{1}{2}\hbar = (\mathcal{J}_x)_{21} \end{aligned}$$

Similarly $(\mathcal{J}_y)_{11} = (\mathcal{J}_y)_{22} = 0$, $(\mathcal{J}_y)_{12} = -i\hbar/2$ and $(\mathcal{J}_y)_{21} = i\hbar/2$. Thus the angular momentum matrices for $j = \frac{1}{2}$ are

$$\begin{aligned} \mathcal{J}_x &= \frac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \mathcal{J}_y = \frac{1}{2}\hbar\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \mathcal{J}_z &= \frac{1}{2}\hbar\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \text{ and } \mathcal{J}^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{aligned} \tag{35}$$

We can also write

$$\mathbf{J} = \tfrac{1}{2}\hbar\sigma \tag{36}$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{37}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \tag{38}$$

and

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{39}$$

are known as Pauli-spin matrices. Further σ_x^2, σ_y^2 and σ_z^2 are all unit matrices. It may be noted that the Pauli spin matrices as well as J_x, J_y, J_z and J^2 are all Hermitian. Further, the eigenvalues of J_x, J_y and J_z are $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. Thus, if we make a measurement of J_x (or J_y or J_z) we will either get $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$.

Now, the simultaneous eigenfunctions of J^2 and J_z are

$$|1\rangle = |\tfrac{1}{2}, \tfrac{1}{2}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{40}$$

and $$|2\rangle = |\tfrac{1}{2}, -\tfrac{1}{2}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{41}$$

which are known as the spin up ($|\uparrow\rangle$) and spin down ($|\downarrow\rangle$) states. They are also denoted by $|\hat{\mathbf{z}}\uparrow\rangle$ and $|\hat{\mathbf{z}}\downarrow\rangle$ states implying that if the electron is in the state (say) $|\hat{\mathbf{z}}\downarrow\rangle$ and if the z-component of the spin angular momentum is measured then the measurement will yield $-\frac{1}{2}\hbar$.

From the matrices representing J_x and J_y, we can calculate the corresponding eigenvalues and eigenvectors and we can immediately see that

$$|\hat{\mathbf{x}}\uparrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}|\hat{\mathbf{z}}\uparrow\rangle + \frac{1}{\sqrt{2}}|\hat{\mathbf{z}}\downarrow\rangle \tag{42}$$

$$|\hat{\mathbf{x}}\downarrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}}|\hat{\mathbf{z}}\uparrow\rangle - \frac{1}{\sqrt{2}}|\hat{\mathbf{z}}\downarrow\rangle \tag{43}$$

Thus if a system is in the $|\hat{\mathbf{x}}\downarrow\rangle$ state and if we make a measurement of J_z then the probability of obtaining the value $+\frac{1}{2}\hbar$ is $\frac{1}{2}$ and the value $-\frac{1}{2}\hbar$ is also $\frac{1}{2}$. This will become more explicit when we discuss the Stern-Gerlach experiment.

Similarly we can write down for the $|\hat{\mathbf{y}}\uparrow\rangle$ and $|\hat{\mathbf{y}}\downarrow\rangle$ states in terms of $|\hat{\mathbf{x}}\uparrow\rangle$ & $|\hat{\mathbf{x}}\downarrow\rangle$ and $|\hat{\mathbf{z}}\uparrow\rangle$ & $|\hat{\mathbf{z}}\downarrow\rangle$ states.

9.4 The Stern-Gerlach Experiment

The quantization of angular momentum (often called as space quantization) was experimentally demonstrated by Stern and Gerlach in 1922. This experiment is considered to be one of the greatest experiments in physics. In this experiment a beam of silver atoms was passed through an inhomogeneous magnetic field. For a silver atom in its ground state, the angular momentum is just the spin angular momentum of the electron* and therefore the magnetic moment of the silver atom is simply that of the electron**. The atoms behaving like magnets of moment μ, will be acted upon by a force given by

$$\mathbf{F} = -\nabla U = \nabla(\mu \cdot \mathbf{B})$$

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*The silver atom has 47 electrons; 46 electrons form a state with $L = 0$ and $S = 0$; i.e., the total angular momentum of the silver atom (in its ground state) is just that due to the last electron.

**The Stern-Gerlach experiment cannot be performed with electrons because of the Lorentz force acting on them (see Problem 9.14).

where $U(= -\boldsymbol{\mu}\cdot\mathbf{B})$ represents the interaction energy. We assume the magnetic field to be predominantly in the z-direction and therefore*

$$\mathbf{F} = \mu_z \nabla B_z \approx \mu_z \frac{\partial B_z}{\partial z}\,\hat{\mathbf{z}} \tag{44}$$

which may be written in the form

$$\mathbf{F} = \mu\cos\theta\,\frac{\partial B_z}{\partial z}\,\hat{\mathbf{z}} \tag{45}$$

where θ is the angle that the direction of the magnetic moment makes with the magnetic field. As the atoms come out of the oven, their magnetic moments would point in every possible direction; so (classically) we should expect all values of θ to be possible. Now, travelling a distance l through the region of the magnetic field, the beam will experience a deflection z given by

$$z = \frac{1}{2}\left(\frac{F_z}{M}\right)t^2 = \frac{1}{2M}\,\mu\cos\theta\,\frac{\partial B}{\partial z}\left(\frac{l}{v}\right)^2 \tag{46}$$

where M is the mass and v the velocity of the atoms. The atomic velocities, although not unique, will range around a mean value v determined by the temperature of the oven.

In the absence of the magnetic field, the beam, defined by the slits, forms a narrow line. When the field is turned on, the line ought to widen continuously in the z-direction, the deflection depending on the value of θ. Thus, classically, the widest deflections will occur for atoms whose magnetic moments are alinged along or opposite the z-direction (i.e., for $\cos\theta = \pm 1$); and for atoms directed horizontally (for which $\cos\theta = 0$) the deflection should be zero. However, when the experiment was performed, the detector recorded a two line pattern showing that the silver beam had split into two components on passing through the inhomogeneous magnetic field. Since the displacement is proportional to μ_z, the result of the above experiment implies that an attempt to measure μ_z could lead to one of the two eigenvalues $+\mu_0$ and $-\mu_0$. Further, since in classical theory, the magnetic moment is proportional to its angular momentum, this result may also be interpreted as evidence of the quantization of angular momentum.

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*We may mention here that the time variation of the spin angular momentum is given by (see Problems 18.8 and 18.9)

$$\frac{d\mathbf{s}}{dt} = \boldsymbol{\mu}\times\mathbf{B} = \gamma\mathbf{s}\times\mathbf{B}$$

where $\gamma(= gq/2m;\ g \simeq 2)$ represents the gyromagnetic ratio. The above equation shows that the components of $\mathbf{s}$ perpendicular to $\mathbf{B}$ will average out to zero whereas the component parallel to $\mathbf{B}$ will remain constant (this is known as the Larmor precession). Thus, although $|\partial B_y/\partial y| \approx |\partial B_z/\partial z|$ (because of the Maxwell equation $\nabla\cdot\mathbf{B} = 0$), since $\mathbf{B}$ is predominantly in the z-direction, we may neglect the terms proportional to μ_x and μ_y in Eq. (44) because they will average out to zero.

It is of interest to mention that if one of the components of the split beam is stopped and the other is allowed to pass through an inhomogeneous field in the z-direction then no further splitting will occur; however, if the inhomogeneous field is in the y-direction then the beam will again split up into two beams corresponding to the $|\hat{\mathbf{y}}\uparrow\rangle$ and $|\hat{\mathbf{y}}\downarrow\rangle$ states (see also Sec. 9.6).

9.5 The Pauli Wave Function and the Pauli Equation

We see, therefore, that the electron is to be endowed with two internal degrees of freedom corresponding to values of $\pm\frac{1}{2}\hbar$ for the component of its intrinsic angular momentum along a specified axis (say the z-axis). Accordingly, we need two wavefunctions to describe the state of an electron at each point in space. Writing them in matrix form, we have

$$\psi_P = \begin{pmatrix} \psi_+(x, y, z) \\ \psi_-(x, y, z) \end{pmatrix} \tag{47}$$

Such single column matrices are known as spinors* and the wavefunction is known as the Pauli wavefunction (hence the subscript p on ψ). Writing

$$\psi_P = \psi_+\chi_+ + \psi_-\chi_- = \psi_+\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \psi_-\begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{48}$$

we say that any spinor can be written as a linear combination of the basic spinors

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\hat{\mathbf{z}}\uparrow\rangle \quad \text{and} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\hat{\mathbf{z}}\downarrow\rangle \tag{49}$$

Thus

$$\int |\psi_+|^2 \, d\tau \quad \text{and} \quad \int |\psi_-|^2 \, d\tau$$

would represent the probabilities of obtaining the $|\hat{\mathbf{z}}\uparrow\rangle$ and $|\hat{\mathbf{z}}\downarrow\rangle$ states respectively and we must have

$$\int |\psi_+|^2 \, d\tau + \int |\psi_-|^2 \, d\tau = 1 \tag{50}$$

Since the electron requires information regarding its spin as well as position co-ordinates, the Pauli wavefunction satisfies the equation

$$i\hbar \frac{\partial}{\partial t}\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = H\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} \tag{51}$$

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*Spinors are characterized by special properties under rotations. We do not wish to leave the impression that they are just single column matrices.

where H represents the Hamiltonian. For the hydrogen atom, in the absence of any interaction other than the Coulomb interaction, H, will be of the form

$$H\psi_p = \left[-\frac{\hbar^2}{2m} \nabla^2 \cdot \mathbf{I} + V(\mathbf{r}) \cdot \mathbf{I} \right] \psi_p \tag{52}$$

where $\mathbf{I}$ is the 2×2 unit matrix. Thus ψ_+ and ψ_- satisfy the same equation and the spin up and spin down states have the same energy (see also Problem 9.12). On the other hand, if we take into account the spin-orbit interaction, H will be of the form

$$H\psi_p = \left[-\frac{\hbar^2}{2m} \nabla^2 \cdot \mathbf{I} + V(\mathbf{r}) \cdot \mathbf{I} + H' \right] \psi_p \tag{53}$$

where (see Sec. 18.5)

$$\begin{aligned} H' &= \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \mathbf{L} \cdot \mathbf{s} \\ &= \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \frac{1}{2} \hbar \left[L_x\sigma_x + L_y\sigma_y + L_z\sigma_z \right] \\ &= \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \frac{1}{2} \hbar \begin{pmatrix} L_z & L_x - iL_y \\ L_x + iL_y & -L_z \end{pmatrix} \end{aligned} \tag{54}$$

which is known as the Pauli operator for H'. Obviously, now the equations for ψ_+ and ψ_- will be coupled (see Problem 9.12) and one has to use perturbation theory to consider the effect of H'. This will be discussed in Problem 11.12.

9.6 Transformation of a Spinor under Rotation

We now wish to see how spinors transform under a rotation of the co-ordinate system. Let us suppose that the spin angular momentum is along the direction $\hat{\mathbf{r}}$, this means that $\sigma \cdot \hat{\mathbf{r}}$ will give the eigenvalue ± 1, $\hat{\mathbf{r}}$ represents the unit vector along $\mathbf{r}$. If the base states are χ_+^r and χ_-^r we have

$$\sigma \cdot \hat{\mathbf{r}} \chi_+^r = \chi_+^r \tag{55a}$$

$$\sigma \cdot \hat{\mathbf{r}} \chi_-^r = -\chi_-^r \tag{55b}$$

We now perform an infinitesimal rotation of the system about an axis along the unit vector $\mathbf{n}$. The direction $\hat{\mathbf{r}}$ now changes to $\hat{\mathbf{r}}'$ where

$$\hat{\mathbf{r}}' = \hat{\mathbf{r}} + \delta\varphi\, \mathbf{n} \times \hat{\mathbf{r}} \tag{56}$$

We have

$$\sigma \cdot \hat{\mathbf{r}}' = \sigma \cdot \hat{\mathbf{r}} + \delta\varphi\, \sigma \cdot \mathbf{n} \times \hat{\mathbf{r}} \tag{57}$$

Now, the Pauli matrices satisfy the equation (see Problem 9.5)

$$[\sigma \cdot \mathbf{A}, \sigma \cdot \mathbf{B}] = 2i\, \sigma \cdot \mathbf{A} \times \mathbf{B} \tag{58}$$

Thus

$$\sigma \cdot \hat{\mathbf{r}}' = \sigma \cdot \hat{\mathbf{r}} - \frac{i}{2}\, \delta\varphi \left[\sigma \cdot \mathbf{n}\, \sigma \cdot \hat{\mathbf{r}} - \sigma \cdot \hat{\mathbf{r}}\, \sigma \cdot \mathbf{n} \right] \tag{59}$$

Thus to first order in $\delta\varphi$, we have

$$\sigma \cdot \hat{\mathbf{r}}' = \left(1 - \frac{i}{2}\, \delta\varphi\, \sigma \cdot \mathbf{n} \right) \sigma \cdot \hat{\mathbf{r}} \left(1 + \frac{i}{2}\, \delta\varphi\, \sigma \cdot \mathbf{n} \right) \tag{90}$$

Equation (60) may now be iterated to give (see Problem 9.8)

$$\sigma \cdot \hat{\mathbf{r}}' = \exp\left(-\frac{i}{2}\, \varphi\, \sigma \cdot \mathbf{n} \right) \sigma \cdot \hat{\mathbf{r}} \exp\left(\frac{i}{2}\, \varphi\, \sigma \cdot \mathbf{n} \right) \tag{61}$$

for a finite rotation φ, where the exponential of the operator is defined through Eq. (72) of chapter 6. Our object is to relate χ_+^r, χ_-^r to states $\chi_+^{r'}$ and $\chi_-^{r'}$ where

$$\sigma \cdot \hat{\mathbf{r}}'\, \chi_\pm^{r'} = \pm\, \chi_\pm^{r'} \tag{62}$$

[cf. Eqs. (55*a*) and (55*b*)]. Multiplying Eq. (61) on the right by $\exp\,[-i/2\, \varphi\, \sigma \cdot \mathbf{n}]\, \chi_\pm^r$ and using Eqs. (55*a*) and (55*b*) we have*

$$\sigma \cdot \hat{\mathbf{r}}' \left[\exp\left(-\frac{i}{2}\, \varphi\, \sigma \cdot \mathbf{n} \right) \right] \chi_\pm^r = \pm \exp\left(-\frac{i}{2}\, \varphi\, \sigma \cdot \mathbf{n} \right) \chi_\pm^r \tag{63}$$

Comparing with Eq. (62) we get

$$\chi_\pm^{r'} = \exp\left(-\frac{i}{2}\, \varphi\, \sigma \cdot \mathbf{n} \right) \chi_\pm^r \tag{64}$$

Clearly, any spinor which is a linear combination of χ_+^r and χ_-^r transforms as above. Since

$$\mathbf{s} = \tfrac{1}{2}\hbar\sigma \tag{65}$$

we may write Eq. (63) as

$$\chi' = \exp\left[-\frac{i}{\hbar}\, \varphi\, \mathbf{s} \cdot \mathbf{n} \right] \chi \tag{66}$$

As an example, if $\hat{\mathbf{z}}'$ is a unit vector in a direction obtained by rotating $\hat{\mathbf{z}}$ about an axis $\mathbf{n}$ by an angle φ, then

$$| \hat{\mathbf{z}}' \uparrow \rangle = \exp\left(-\frac{i}{2} \varphi\, \sigma \cdot \mathbf{n} \right) | \hat{\mathbf{z}} \uparrow \rangle \tag{67}$$

$$= \begin{pmatrix} \cos \varphi/2 & -in_z \sin \varphi/2 \\ -in_x + n_y & \sin \varphi/2 \end{pmatrix} \tag{68}$$

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*Here we have used the fact that

$$e^A e^B = e^{A+B}$$

if *A* and *B* commute (see Problem 8.26).

where in the last step we have used some properties of the Pauli matrices (see Problem 9.6) and the fact that

$$|\hat{\mathbf{z}}\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{69}$$

If the rotation is about the y-axis then $n_x = n_z = 0$ and $n_y = 1$, and we may write (see also Problem 9.7)

$$|\hat{\mathbf{z}}'\uparrow\rangle = \begin{pmatrix} \cos\varphi/2 \\ \sin\varphi/2 \end{pmatrix} = \cos\varphi/2\,|\hat{\mathbf{z}}\uparrow\rangle + \sin\varphi/2\,|\hat{\mathbf{z}}\downarrow\rangle \tag{70}$$

showing that if the spin is in the $\hat{\mathbf{z}}'$ direction then the probability of measuring the spin in the $|\hat{\mathbf{z}}\uparrow\rangle$ and $|\hat{\mathbf{z}}\downarrow\rangle$ states are $\cos^2\varphi/2$ and $\sin^2\varphi/2$ respectively. Similarly

$$|\hat{\mathbf{z}}'\downarrow\rangle = \begin{pmatrix} -\sin\varphi/2 \\ \cos\varphi/2 \end{pmatrix} = -\sin\varphi/2\,|\hat{\mathbf{z}}\uparrow\rangle + \cos\varphi/2\,|\hat{\mathbf{z}}\downarrow\rangle \tag{71}$$

Using Eqs. (70) and (71), we can also write

$$|\hat{\mathbf{z}}\uparrow\rangle = \cos\varphi/2\,|\hat{\mathbf{z}}'\uparrow\rangle - \sin\varphi/2\,|\hat{\mathbf{z}}'\downarrow\rangle \tag{72}$$

and

$$|\hat{\mathbf{z}}\downarrow\rangle = \sin\varphi/2\,|\hat{\mathbf{z}}'\uparrow\rangle + \cos\varphi/2\,|\hat{\mathbf{z}}'\downarrow\rangle \tag{73}$$

Now, in the Stern-Gerlach experiment (see Sec. 9.4 and Fig. 1.8) we apply the inhomogeneous field in z-direction and obtain two beams. If we block one of the beams then we get a beam in which the atoms are in the $|\hat{\mathbf{z}}\uparrow\rangle$ state. We next apply another inhomogeneous field in a direction which makes an angle φ with the z-axis and $\pi/2 - \varphi$ with the y-axis; we will then obtain two beams with intensities proportional to $\cos^2\varphi/2$ and $\sin^2\varphi/2$. It is worthwhile mentioning that if the inhomogeneity is in the y-direction then $\varphi = \pi/2$ and the two spots will be of equal intensity. This also follows from the fact that

$$|\hat{\mathbf{z}}\uparrow\rangle = \frac{1}{\sqrt{2}}\Big[\,|\hat{\mathbf{y}}\uparrow\rangle - |\hat{\mathbf{y}}\downarrow\rangle\Big] \tag{74}$$

Returning to Eq. (66), one may notice the resemblance of the transformations of the space wave function (see Eq. 91 of Chapter 6) and the spinors. The eigenfunctions of angular momenta, orbital and spin, can always be written as a linear combination of the products

$$\Phi = Y_{lm_l}\,\chi(m_s) \tag{75}$$

where we have introduced the notation

$$\chi(\tfrac{1}{2}) = \chi_+ \quad \text{and} \quad \chi(-\tfrac{1}{2}) = \chi_- \tag{76}$$

Thus under rotation $\Phi \rightarrow \Phi'$ where

$$\Phi' = \exp\left[-\frac{i}{\hbar}\varphi(\mathbf{L} + \mathbf{s}) \cdot \mathbf{n}\right]\Phi \tag{77}$$

The operator $\mathbf{J} = \mathbf{L} + \mathbf{s}$ is the total angular momentum.

PROBLEMS

Problem 9.1

In Sec. 9.3 we had derived the angular momentum matrices corresponding to $j = \frac{1}{2}$ in a representation in which J^2 and J_z are diagonal. Carry out a similar analysis for $j = 1$ and $j = 3/2$.

Problem 9.2

For an eigenstate of J^2 and J_z show that

$$\langle J_x \rangle = \langle J_y \rangle = 0 \tag{78}$$

and

$$\langle J_x^2 \rangle = \langle J_y^2 \rangle = \tfrac{1}{2}\hbar^2 [j(j+1) - m^2] \tag{79}$$

From the above results develop a classical model for angular momentum.

Problem 9.3

In Sec. 9.3 we had derived the angular momentum matrices in a representation in which J^2 and J_z are diagonal. Carry out a similar analysis in a representation in which J^2 and J_x are diagonal; assume $j = \frac{1}{2}$.

Problem 9.4

Show that the Pauli spin matrices satisfy the relation

$$\sigma_i \sigma_j = \delta_{ij} + i\varepsilon_{ijk}\, \sigma_k \tag{80}$$

where ε_{ijk}, which is known as the totally anti-symmetric unit tensor, is defined by

$$\varepsilon_{123} = \varepsilon_{231} = \varepsilon_{312} = 1 \qquad \text{(cyclic indices)}$$

$$\varepsilon_{321} = \varepsilon_{213} = \varepsilon_{132} = -1 \qquad \text{(anticyclic indices)}$$

with all other components equal to zero.

Problem 9.5

Using Eq. (80) show

$$(\sigma \cdot \mathbf{A})\, (\sigma \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i\sigma \cdot (\mathbf{A} \times \mathbf{B}) \tag{81}$$

where $\mathbf{A}$ and $\mathbf{B}$ are arbitrary vectors. Thus

$$(\sigma \cdot \mathbf{n})^2 = 1 \tag{82}$$

where $\mathbf{n}$ is an arbitrary unit vector.

PROBLEM 9.6

Using Eq. (82) show that

$$\exp\left[-\frac{i}{2}\varphi\,\boldsymbol{\sigma}\cdot\mathbf{n}\right] = \cos\varphi/2 - i(\boldsymbol{\sigma}\cdot\mathbf{n})\sin\varphi/2 \tag{83}$$

and thereby prove Eq. (68).

PROBLEM 9.7

Consider a rotation about the y-axis through an angle φ. Assuming that the components of the spin angular momentum transform as ordinary vectors, prove Eqs. (72) and (73).

PROBLEM 9.8

From Eqs. (59) and (60) derive Eq. (61).

PROBLEM 9.9

Obtain the eigenvalues and eigenvectors of σ_x and σ_y and express them as linear combinations of $|\hat{\mathbf{z}}\uparrow\rangle$ and $|\hat{\mathbf{z}}\downarrow\rangle$ states. Give a physical interpretation.

PROBLEM 9.10

Discuss the outcome of a Stern-Gerlach type of experiment for a system corresponding to a spin angular momentum of $\hbar$. Show the existence of three spots on the screen. [This experiment has been very nicely discussed by Feynmann *et al.* (1964) Vol. III, Chapter 5.]

PROBLEM 9.11

From Eqs. (30) and (31) it immediately follows that

$$L_\pm\, Y_{l_m}(\theta,\varphi) = \hbar\,[(l\mp m)(l\pm m+1)]^{1/2}\, Y_{l,\,m\pm 1}(\theta,\varphi) \tag{84}$$

where

$$L_\pm = L_x \pm iL_y \tag{85}$$

Thus for a state whose angular part is $Y_{l_m}(\theta,\varphi)$, show that

$$\langle L_z\rangle = m\hbar,\ \langle L_x\rangle = \langle L_y\rangle = 0$$

and

$$\langle L_x^2\rangle = \langle L_y^2\rangle = \tfrac{1}{2}\hbar^2\,(l^2+l-m^2) \tag{86}$$

PROBLEM 9.12

(*a*) For a hydrogen like atom, neglecting the spin orbit interaction, construct eigenstates which are simultaneous eigenstates of H, L^2, L_z and s_z.

(*b*) Introduce the total angular momentum operator

$$\mathbf{J} = \mathbf{L} + \mathbf{s} = \begin{pmatrix} \mathbf{L} & 0 \\ 0 & \mathbf{L} \end{pmatrix} + \tfrac{1}{2}\hbar\,\boldsymbol{\sigma} \tag{87}$$

construct states which are simultaneous eigenstates of J_z, L^2, s^2 and J^2. These states will be such that H' [which represents the spin orbit interaction, see Eq. (54)] will be diagonal in this representation and degenerate state perturbation theory can be used to study the effect of the spin orbit interaction (see Problem 11.12). See also Problem 18.3.

PROBLEM 9.13

In the Stern-Gerlach experiment, for the beam to produce two distinguishable spots, the diffraction divergence must be small compared to the splitting due to inhomogeneous magnetic field. Show that this leads to the condition

$$\left|\frac{\partial B}{\partial z}\right| \gg \frac{8\pi m}{q\Delta z}$$

where Δz is the distance between the pole pieces of the magnet.

PROBLEM 9.14

Show that the Stern-Gerlach experiment cannot be performed for an electron. (Assume $\partial B_x/\partial x = 0$ and consider the effect of the Lorentz force acting in the z-direction.)

SOLUTIONS

SOLUTION 9.1

For $j = 1$, we have $m = +1, 0$ or -1. The three base states, which are simultaneous eigenstates of J^2 and J_z, are

$$|1\rangle = |1, 1\rangle, |2\rangle = |1, 0\rangle \text{ and } |3\rangle = |1, -1\rangle$$

Now using Eqs. (29)–(31) we get

$$\langle j', m' | \mathcal{J}_+ | j, m\rangle = [(j + m + 1)(j - m)]^{1/2}\, \hbar\, \delta_{jj'}\, \delta_{m'\, m+1}$$

and

$$\langle j', m' | \mathcal{J}_- | j, m\rangle = [(j + m)(j - m + 1)]^{1/2}\, \hbar\, \delta_{jj'}\, \delta_{m'\, m-1}$$

Since $\mathcal{J}_x = \frac{1}{2}(\mathcal{J}_+ + \mathcal{J}_-)$ we get

$$(\mathcal{J}_x)_{12} = \langle 1 | \mathcal{J}_x | 2\rangle = \frac{1}{\sqrt{2}}\, \hbar = (\mathcal{J}_x)_{21} = (\mathcal{J}_x)_{32} = (\mathcal{J}_x)_{23}$$

and all the other matrix elements are zero. Similarly, we can calculate for J_y. Obviously $\mathcal{J}^2$ and $\mathcal{J}_z$ will be diagonal. Tables 9.1 to 9.4 (adapted from Newing and Cunningham, 1967) give the angular momentum matrices. Notice the Pauli matrices corresponding to $j = \frac{1}{2}$ and that the matrices for $\mathcal{J}_z$ and $\mathcal{J}^2$ are diagonal, the diagonal elements representing the eigenvalues of the corresponding operator.

TABLE 9.1

$$
2J_x/\hbar \qquad
\begin{array}{cc|cccccccccc}
j & & 0 & 1/2 & 1/2 & 1 & 1 & 1 & 3/2 & 3/2 & 3/2 & 3/2 \\
 & m & 0 & 1/2 & -1/2 & 1 & 0 & -1 & 3/2 & 1/2 & -1/2 & -3/2 \\
\hline
0 & 0 & 0 & & & & & & & & & \\
1/2 & 1/2 & & 0 & 1 & & & & & & & \\
1/2 & -1/2 & & 1 & 0 & & & & & & & \\
1 & 1 & & & & 0 & \sqrt{2} & 0 & & & & \\
1 & 0 & & & & \sqrt{2} & 0 & \sqrt{2} & & & & \\
1 & -1 & & & & 0 & \sqrt{2} & 0 & & & & \\
3/2 & 3/2 & & & & & & & 0 & \sqrt{3} & 0 & 0 \\
3/2 & 1/2 & & & & & & & \sqrt{3} & 0 & 2 & 0 \\
3/2 & -1/2 & & & & & & & 0 & 2 & 0 & \sqrt{3} \\
3/2 & -3/2 & & & & & & & 0 & 0 & \sqrt{3} & 0 \\
\cdot & \cdot & & & & & & & & & & \\
\cdot & \cdot & & & & & & & & & & \\
\cdot & \cdot & & & & & & & & & &
\end{array}
$$

TABLE 9.2

$$
2J_y\hbar \qquad
\begin{array}{cc|cccccccccc}
j & & 0 & 1/2 & 1/2 & 1 & 1 & 1 & 3/2 & 3/2 & 3/2 & 3/2 \\
 & m & 0 & 1/2 & -1/2 & 1 & 0 & -1 & 3/2 & 1/2 & -1/2 & -3/2 \\
\hline
0 & 0 & 0 & & & & & & & & & \\
1/2 & 1/2 & & 0 & -i & & & & & & & \\
1/2 & -1/2 & & i & 0 & & & & & & & \\
1 & 1 & & & & 0 & -i\sqrt{2} & 0 & & & & \\
1 & 0 & & & & i\sqrt{2} & 0 & -i\sqrt{2} & & & & \\
1 & -1 & & & & 0 & i\sqrt{2} & 0 & & & & \\
3/2 & 3/2 & & & & & & & 0 & -i\sqrt{3} & 0 & 0 \\
3/2 & 1/2 & & & & & & & i\sqrt{3} & 0 & -2i & 0 \\
3/2 & -1/2 & & & & & & & 0 & 2i & 0 & -i\sqrt{3} \\
3/2 & -3/2 & & & & & & & 0 & 0 & i\sqrt{3} & 0 \\
\cdot & \cdot & & & & & & & & & & \\
\cdot & \cdot & & & & & & & & & &
\end{array}
$$

TABLE 9.3

$J_z/\hbar^2$

j		0	1/2	1/2	1	1	1	3/2	3/2	3/2	3/2
	m	0	1/2	−1/2	1	0	−1	3/2	1/2	−1/2	−3/2
0	0	0									
1/2	1/2		1/2	0							
1/2	−1/2		0	−1/2							
1	1				1	0	0				
1	0				0	0	0				
1	−1				0	0	−1				
3/2	3/2							3/2	0	0	0
3/2	1/2							0	1/2	0	0
3/2	−1/2							0	0	−1/2	0
3/2	−3/2							0	0	0	−3/2

TABLE 9.4

$J^2/\hbar^2$

j		0	1/2	1/2	1	1	1	3/2	3/2	3/2	3/2
	m	0	1/2	−1/2	1	0	−1	3/2	1/2	−1/2	−3/2
0	0	0									
1/2	1/2		3/4	0							
1/2	−1/2		0	3/4							
1	1				2	0	0				
1	0				0	2	0				
1	−1				0	0	2				
3/2	3/2							15/4	0	0	0
3/2	1/2							0	15/4	0	0
3/2	−1/2							0	0	15/4	0
3/2	−3/2							0	0	0	15/4

SOLUTION 9.2

$$\langle j, m \mid J_x \mid j, m \rangle = \tfrac{1}{2}\langle j, m \mid J_+ \mid j, m \rangle + \tfrac{1}{2}\langle j, m \mid J_- \mid j, m \rangle = 0$$

(using Eqs. 29–31)

$$\begin{aligned}\langle j, m \mid J_x^2 \mid j, m \rangle &= \tfrac{1}{2}[\langle j, m \mid J_+ J_+ \mid j, m \rangle + \langle j, m \mid J_+ J_- \mid j, m \rangle \\ &\quad + \langle j, m \mid J_- J_+ \mid j, m \rangle + \langle j, m \mid J_- J_- \mid j, m \rangle] \\ &= \tfrac{1}{2}[0 + \{(j+m)(j-m+1)\}^{1/2} \langle j, m \mid J_+ \mid j, m+1 \rangle \\ &\quad + \{(j-m)(j+m+1)\}^{1/2} \langle j, m \mid J_- \mid j, m+1 \rangle + 0] \\ &= \tfrac{1}{2}\hbar^2[j(j+1) - m^2] \qquad (88)\end{aligned}$$

etc. Obviously

$$\langle j, m \mid J_z^2 \mid j, m \rangle = m^2\hbar^2 \qquad (89)$$

and

$$\langle j, m \mid J^2 \mid j, m \rangle = j(j+1)\hbar^2 \qquad (90)$$

From the above equations we can develop a classical model for angular momentum. The total angular momentum vector OP [whose length is assumed to be $\sqrt{j(j+1)}\,\hbar$] is assumed to precess about the z-axis (see Fig. 9.1). As it precesses, the z component of OP ($= OQ$) remains constant, which we assume to be equal to $m\hbar$. The x and y components of OP change with time and their average value is zero. Now

$$PQ^2 = j(j+1)\,\hbar^2 - m^2\hbar^2$$

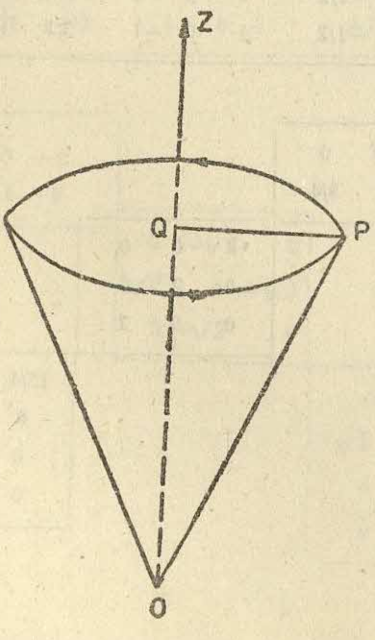

Fig. 9.1. A classical model for the angular momentum vector.

represents $\langle \mathcal{J}_x^2 \rangle + \langle \mathcal{J}_y^2 \rangle$ consistent with Eq. (88). Thus for the state $| j, m \rangle$ we may assume the total angular momentum vector precessing about the z-axis.

SOLUTION 9.3

$$\mathcal{J}_x = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \mathcal{J}_y = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \mathcal{J}_z = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

SOLUTION 9.4

The following properties of the Pauli matrices are easily established

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1 \tag{91}$$

$$\sigma_x \sigma_y = i\sigma_z, \text{ etc.} \tag{92}$$

$$\sigma_x \sigma_y + \sigma_y \sigma_x = 0, \text{ etc.} \tag{93}$$

from which Eq. (80) immediately follows.

SOLUTION 9.5

$$(\sigma \cdot \mathbf{A})(\sigma \cdot \mathbf{B}) = \sum_{ij} \sigma_i \mathbf{A}_i \sigma_j \mathbf{B}_j = (\mathbf{A} \cdot \mathbf{B}) + i\sigma \cdot (\mathbf{A} \times \mathbf{B}) \tag{94}$$

as can be verified by expanding the RHS and using Eqs. (91)–(93).

SOLUTION 9.6

$$\exp\left(-\frac{i\varphi}{2}\sigma\cdot\mathbf{n}\right) = \sum_{r=0,1,\ldots}\left(-\frac{i\varphi}{2}\right)^r \frac{(\sigma\cdot\mathbf{n})^r}{r!}$$

$$= \sum_{r=0,2,4\ldots} \frac{\left(-\frac{i\varphi}{2}\right)^r}{r!} + (\sigma\cdot\mathbf{n}) \sum_{r=1,3,5\ldots} \frac{(-i\varphi/2)^r}{r!}$$

(using Eq. 82)

$$= \cos\varphi/2 - i(\sigma\cdot\mathbf{n})\sin\varphi/2$$

Thus

$$\exp\left(-\frac{i\varphi}{2}\sigma\cdot\mathbf{n}\right)|\hat{z}\uparrow\rangle = \cos\varphi/2\begin{pmatrix}1\\0\end{pmatrix} - i\sin\frac{\varphi}{2}\left[n_x\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} + n_y\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} + n_z\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}\right]$$

which gives Eq. (68).

SOLUTION 9.7

For a rotation about the y-axis through an angle φ, the co-ordinates transform according to the following equations (cf. Eq. 66 of Chapter 6):

$$\begin{aligned} x' &= x\cos\varphi - z\sin\varphi \\ y' &= y \\ z' &= x\sin\varphi + z\cos\varphi \end{aligned} \tag{95}$$

Thus

$$\begin{aligned} s_z' &= s_x\sin\varphi + s_z\cos\varphi \\ &= \tfrac{1}{2}\hbar\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\sin\varphi + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\cos\varphi\right] \\ &= \tfrac{1}{2}\hbar\begin{pmatrix} \cos\varphi & \sin\varphi \\ \sin\varphi & -\cos\varphi \end{pmatrix} \end{aligned}$$

The eigenvalues of $s_{z'}$ are obviously $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$; the eigenvector corresponding to $+\frac{1}{2}\hbar$ being

$$|\hat{z}'\uparrow\rangle = \begin{pmatrix} \cos\varphi/2 \\ \sin\varphi/2 \end{pmatrix} = \cos\varphi/2\,|\hat{z}\uparrow\rangle + \sin\varphi/2\,|\hat{z}\downarrow\rangle$$

consistent with Eq. (70).

SOLUTION 9.8

By rotating the system through an angle φ, let the vector $\hat{r}(0)$ change to $\hat{r}(\varphi)$. If on subsequent rotation $\Delta\varphi$ the vector becomes $\hat{r}(\varphi + \Delta\varphi)$ then, using Eq. (59) we have

$$\sigma\cdot\hat{r}(\varphi+\Delta\varphi) = \sigma\cdot\hat{r}(\varphi) - \frac{i}{2}\Delta\varphi\left[\sigma\cdot n\,\sigma\cdot\hat{r}(\varphi) - \sigma\cdot\hat{r}(\varphi)\,\sigma\cdot n\right]$$

which can be written in the form

$$\frac{F(\varphi+\Delta\varphi) - F(\varphi)}{\Delta\varphi} = \frac{dF}{d\varphi} = -\frac{i}{2}\left[\sigma\cdot n\,F(\varphi) - F(\varphi)\,\sigma\cdot n\right]$$

where $F(\varphi) = \sigma\cdot\hat{r}(\varphi)$. The solution of the above equation is

$$F(\varphi) = \exp\left[-\frac{i}{2}\varphi\,\sigma\cdot n\right]F(0)\exp\left[\frac{i}{2}\varphi\,\sigma\cdot n\right] \tag{96}$$

as can be verified by differentiating the above equation. Equation (96) is identical to Eq. (61).

SOLUTION 9.12

(*a*) Since the $|\hat{z}\uparrow\rangle$ and $|\hat{z}\downarrow\rangle$ states are represented by

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

respectively, the state which is a simultaneous eigenstate of H, L^2, L_z and s_z [belonging to the eigenvalues E_n, $l(l+1)\hbar^2$, $m\hbar$ and $\frac{1}{2}\hbar$] is given by

$$\psi_{nlm}|\hat{z}\uparrow\rangle = \begin{pmatrix} \psi_{nlm} \\ 0 \end{pmatrix} \tag{97}$$

Similarly the state for which the corresponding eigenvalues are E_n, $l(l+1)\hbar^2$, $m\hbar$ and $-\frac{1}{2}\hbar$ would be

$$\psi_{nlm}|\hat{z}\downarrow\rangle = \begin{pmatrix} 0 \\ \psi_{nlm} \end{pmatrix} \tag{98}$$

In the absence of spin orbit interaction, both the spin up and spin down states have the same energy.

(*b*) The Pauli operator for J_z is

$$(J_z)_p = \begin{pmatrix} L_z & 0 \\ 0 & L_z \end{pmatrix} + \tfrac{1}{2}\hbar\,\sigma_z = \begin{pmatrix} L_z + \frac{1}{2}\hbar & 0 \\ 0 & L_z - \frac{1}{2}\hbar \end{pmatrix}$$

Thus, if we write the eigenvalue equation as

$$\begin{pmatrix} L_z + \frac{1}{2}\hbar & 0 \\ 0 & L_z - \frac{1}{2}\hbar \end{pmatrix}\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = m_j\hbar\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}$$

then

$$L_z\,\psi_+ = (m_j - \tfrac{1}{2})\hbar\psi_+$$

and

$$L_z\,\psi_- = (m_j + \tfrac{1}{2})\hbar\psi_-$$

If we now replace L_z by $-i\hbar\,\partial/\partial\varphi$, we obtain the following φ-dependences of ψ_+ and ψ_-

$$\psi_+ \sim \exp[i(m_j - \tfrac{1}{2})\varphi]$$

$$\psi_- \sim \exp[i(m_j + \tfrac{1}{2})\varphi]$$

Further, for L^2 to have the value $l(l+1)\hbar^2$, we must have

$$L^2\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = l(l+1)\hbar^2\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}$$

or,

$$\psi_+ = C_+\,R_{nl}(r)\,Y_{l\,m_j-\frac{1}{2}}\quad(\theta,\varphi)$$

and

$$\psi_- = C_-\,R_{nl}(r)\,Y_{l\,m_j+\frac{1}{2}}\quad(\theta,\varphi)$$

Clearly $m_j - \frac{1}{2}$ must be an integer or zero. Since s^2 is $\frac{3}{4}\hbar^2$ times a unit matrix, the vector $\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}$ is also an eigenstate of s^2. Finally,

$$(\mathcal{J}^2)_P = (L^2)_p + s^2 + 2\,\mathbf{L}\cdot\mathbf{s}$$
$$= \begin{pmatrix} L^2 & 0 \\ 0 & L^2 \end{pmatrix} + \tfrac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \hbar \begin{pmatrix} L_z & L_x - iL_y \\ L_x + iL_y & -L_z \end{pmatrix}$$

We write the eigenvalue equation for $\mathcal{J}^2$ as

$$(\mathcal{J}^2)_P \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = j(j+1)\hbar^2 \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}$$

where $j(j+1)\hbar^2$ represents the eigenvalues of $\mathcal{J}^2$ (j is still to be determined!). On substitution, we obtain

$$[L^2 + \tfrac{3}{4}\hbar^2 + \hbar L_z - j(j+1)\hbar^2]\, C_+ R_{nl}\, Y_{l\, m_j - 1/2} + \hbar L_- [C_- R_{nl}\, Y_{l\, m_j + 1/2}] = 0$$

and

$$\hbar L_+ [C_+ R_{nl}\, Y_{l m_j - 1/2}] + [L^2 + \tfrac{3}{4}\hbar^2 - \hbar L_z - j(j+1)\hbar^2]\, [C_+ R_{nl}\, Y_{l\, m_{j+1/2}}] = 0$$

or

$$[l(l+1) + \tfrac{3}{4} + (m_j - \tfrac{1}{2}) - j(j+1)]\, C_+$$
$$+ [(l + m_j + \tfrac{1}{2})(l - m_j + \tfrac{1}{2})]^{1/2}\, C_- = 0$$

and

$$[(l - m_j + \tfrac{1}{2})(l + m_j + \tfrac{1}{2})]^{\frac{1}{2}}\, C_+ + [l(l+1) + \tfrac{3}{4} - (m_j + \tfrac{1}{2}) - j(j+1)]\, C_- = 0$$

For nontrivial solutions, we must have

$$[l(l+1) - j(j+1) + \tfrac{1}{4}]^2 - m_j^2 = (l + \tfrac{1}{2})^2 - m_j^2$$

or $\quad j(j+1) = l(l+1) + \frac{1}{4} \pm (l + \frac{1}{2})$

$$\text{which gives } j = l + \tfrac{1}{2} \quad \text{or} \quad l - \tfrac{1}{2} \tag{99}$$

(This is consistent with the results that will be obtained in Sec. 10.2). Corresponding to each value of j, the ratio C_+/C_- can be determined and if we use the normalization condition given by Eq. (50), we would obtain the following expressions for the Pauli wavefunction

$$\psi(n, l, j = l + \tfrac{1}{2}, m_j) = \begin{pmatrix} \left(\dfrac{l + \frac{1}{2} + m_j}{(2l+1)}\right)^{1/2} R_{nl}(r)\, Y_{l\, m_j - \frac{1}{2}}(\theta, \varphi) \\ \left(\dfrac{l + \frac{1}{2} - m_j}{2l+1}\right)^{1/2} R_{nl}(r)\, Y_{l\, m_j + \frac{1}{2}}(\theta, \varphi) \end{pmatrix} \tag{100}$$

$$l = 0, 1, 2 \ldots (n-1)$$
$$m_j = -l - \tfrac{1}{2}, \ldots l + \tfrac{1}{2}$$

and

$$\psi(n, l, j = l - \tfrac{1}{2}, m_j) = \begin{pmatrix} -\left(\dfrac{l+\frac{1}{2}-m_j}{2l+1}\right)^{1/2} R_{nl}(r)\, Y_{l\, m_j-\frac{1}{2}}(\theta, \varphi) \\ \left(\dfrac{l+\frac{1}{2}+m_j}{2l+1}\right)^{1/2} R_{nl}(r)\, Y_{l\, m_j+\frac{1}{2}}(\theta, \varphi) \end{pmatrix} \tag{101}$$

$$l = 1, 2, \ldots\ldots, n-1$$
$$m_j = -l + \tfrac{1}{2}, \ldots, l + \tfrac{1}{2}$$

The above expressions can also be directly obtained by using Table 10.1 for the Clebsch-Gordan coefficients.

SOLUTION 9.13

The force acting on the atom in the z-direction is given by [see Eq. (44)]

$$F_z = \mu_z \frac{\partial B}{\partial z} \tag{102}$$

where μ_z is the magnetic moment in the z-direction. Since the magnetic moment of the silver atom is just that of the spin of the electron, we have (for the beam going upwards)

$$\mu_z = \gamma s_z = \frac{gq}{2m} \tfrac{1}{2}\hbar \tag{103}$$

where $\gamma(= gq/2m, g \simeq 2)$ is the gyromagnetic ratio, m is the mass of the electron. Thus, the angular displacement Φ (see Fig. 1.8) is approximately given by

$$\Phi \simeq \frac{\frac{1}{2}\left(\dfrac{F_z}{M}\right)t^2}{\left(\dfrac{p_x}{M}\right)t} \approx \tfrac{1}{2}\left|\frac{q}{m}\ \frac{\partial B}{\partial z}\right| (\tfrac{1}{2}\hbar)\ \frac{t}{p_x} \tag{104}$$

where t is the time that the atom (of mass M) spends inside the magnet and p_x represents the initial momentum. Now, the diffraction divergence in the z-direction is approximately given by

$$\Delta\Phi \sim \frac{\lambda}{\Delta z} \sim \frac{h}{p_x \Delta z} \tag{105}$$

For the two beams to produce distinguishable spots (i.e., without any overlap), we must have $\Phi \gg \Delta\Phi$ or

$$\left|\frac{\partial B}{\partial z}\right| \gg \frac{8\pi\, m}{q\Delta z} \tag{106}$$

SOLUTION 9.14

The magnetic field satisfies the equation

$$\nabla \cdot \mathbf{B} = \frac{\partial B_x}{\partial x} + \frac{\partial B_y}{\partial y} + \frac{\partial B_z}{\partial z} = 0$$

Assuming no variation in the x direction, we have

$$\frac{\partial B_y}{\partial y} = -\frac{\partial B_z}{\partial z} \tag{107}$$

For an electron there will be a Lorentz force whose magnitude in the z-direction will be $p_x\, B_y q/m$; thus the angular deflection will be (see Eq. 104)

$$\Theta \sim \frac{\frac{1}{2}\left(\frac{q}{m}\, p_x\, B_y\right)\frac{1}{m}\, t^2}{\left(\frac{p_x}{m}\right) t} \sim \frac{q}{2m}\, t\, B_y$$

or the spread in Θ would be

$$\Delta\Theta \sim \frac{q}{2m}\, t\, \frac{\partial B_y}{\partial y}\, \Delta y \sim \frac{q}{2m}\, t \left|\frac{\partial B_z}{\partial z}\right| \Delta y \sim \frac{p_x\, \Phi}{\hbar}\, \frac{h}{\Delta p_y}$$

since $\Delta p_y \ll p_x$, we have $\Delta\Theta \gg \Phi$ implying that the spreading due to Lorentz force will dominate and therefore the Stern-Gerlach experiment cannot be performed with electrons. However, for electrically neutral particles, there is no Lorentz force.

CHAPTER TEN

Addition of Angular Momenta—The Clebsch-Gordan Coefficients

10.1 Introduction

When a system is made up of composite parts which interact with each other, it is the total angular momentum which is conserved and is of great importance. Indeed, the angular momenta to be combined may pertain to the same particle, namely, its orbital and spin angular momenta; or may pertain to the orbital angular momenta of two different particles.

As an example, we consider the hydrogen atom problem. If we include the spin-orbit interaction, the Hamiltonian is given by (see Problem 11.12 and Sec. 18.5)

$$H = H_0 + H' \tag{1}$$

where

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

$$H' = \xi(r)\,\mathbf{L}\cdot\mathbf{s} = \xi(r)\,(L_x s_x + L_y s_y + L_z s_z)$$

and

$$\xi(r) = \frac{Ze^2}{2m^2c^2}\,\frac{1}{r^3}$$

It can be immediately seen that whereas L_z and s_z commute with H_0, they do not commute with H'. Indeed,

$$\begin{aligned}[L_z, H] &= [L_z, H_0] + [L_z, H'] \\ &= \xi(r)\,([L_z, L_x]\,s_x + [L_z, L_y]\,s_y + [L_z, L_z]\,s_z) \\ &= i\hbar\,\xi(r)\,(L_y s_x - L_x s_y)\end{aligned}$$

where we have used the results of Sec. 6.5. Thus L_z does not commute with H. Similarly

$$[s_z, H] = i\hbar\,\xi(r)\,(L_x s_y - L_y s_x) = -[L_z, H]$$

immediately giving

$$[J_z, H] = 0 \tag{2}$$

where $J_z = L_z + s_z$ represents the z-component of the total angular momentum operator. Thus J_z (and similarly J_x and J_y) commute with H and are constants of motion.

We next consider the helium atom, the Hamiltonian of which is given by (see Sec. 15.2).

$$H = H_0 + H' \tag{3}$$

where

$$H_0 = -\frac{\hbar^2}{2m}\left[\nabla_1^2 + \nabla_2^2\right] - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}$$

and

$$H' = \frac{e^2}{r_{12}} = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Once again L_{1z} and L_{2z} commute with H_0 but do not commute with H'; indeed

$$[L_z, H] = [L_{1z} + L_{2z}, H] = 0 \tag{4}$$

implying that the components of the total angular momentum are constants of motion.

In this chapter we will consider the addition of angular momenta quite generally. Let $\mathbf{J}_1$ and $\mathbf{J}_2$ denote two angular momentum operators satisfying the commutation relations (see Eq. 3 of Chapter 9).

$$\begin{aligned} [J_{1x}, J_{1y}] &= iJ_{1z} \\ [J_{2x}, J_{2y}] &= iJ_{2z} \end{aligned} \tag{5}$$

and other equations can be written in cyclic order.* We also have

$$[J_1^2, J_{1x}] = 0 = [J_2^2, J_{2x}] \text{ etc.}$$

We assume that the components of $\mathbf{J}_1$ and $\mathbf{J}_2$ commute with each other, i.e.,

$$[J_{1x}, J_{2x}] = 0 = [J_{1x}, J_{2y}] \text{ etc.}$$

We define the total angular momentum operator $\mathbf{J}$:

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2 \tag{6}$$

Now

$$\begin{aligned} [J_y, J_z] &= J_yJ_z - J_zJ_y \\ &= (J_{1y} + J_{2y})(J_{1z} + J_{2z}) - (J_{1z} + J_{2z})(J_{1y} + J_{2y}) \\ &= (J_{1y}J_{1z} - J_{1z}J_{1y}) + (J_{2y}J_{2z} - J_{2z}J_{2y}) \\ &= i(J_{1x} + J_{2x}) = iJ_x \end{aligned} \tag{7}$$

---

*Often the commutation relations are written in the following form

$$\mathbf{J} \times \mathbf{J} = i\mathbf{J}$$

because

$$(\mathbf{J} \times \mathbf{J})_x = J_yJ_z - J_zJ_y = iJ_x \text{ etc.}$$

implying that the components of **J** satisfy the same commutation relations as that of an angular momentum operator. Thus (see also Problem 10.1)

$$[\mathcal{J}^2, \mathcal{J}_z] = 0 \text{ etc.,} \tag{8}$$

here

$$\begin{aligned} \mathcal{J}^2 &= \mathcal{J}_x^2 + \mathcal{J}_y^2 + \mathcal{J}_z^2 = (\mathcal{J}_{1x} + \mathcal{J}_{2x})^2 + \dots + \dots \\ &= \mathcal{J}_1^2 + \mathcal{J}_2^2 + 2\,\mathbf{J}_1 \cdot \mathbf{J}_2 \end{aligned} \tag{9}$$

where we have used the relation $\mathbf{J}_1 \cdot \mathbf{J}_2 = \mathbf{J}_2 \cdot \mathbf{J}_1$ because components of $\mathbf{J}_1$ commute with components of $\mathbf{J}_2$. Since the total angular momentum vector is a constant of motion we will, in this chapter, construct vectors which are simultaneous eigenvectors of $\mathcal{J}^2$ and $\mathcal{J}_z$.

Let $\psi_1(j_1, m_1)$ be the simultaneous eigenvector of J_1^2 and J_{1z}, i.e.,

$$\mathcal{J}_1^2\psi_1(j_1, m_1) = j_1(j_1 + 1)\, \psi_1(j_1, m_1) \tag{10}$$

and $\quad \mathcal{J}_{1z}\psi_1(j_1, m_1) = m_1\psi_1(j_1, m_1)$

[see Eqs. (5) and (6) of Chapter 9]. We are using the atomic units where $\hbar = 1$. Similarly let $\psi_2(j_2, m_2)$ represent the simultaneous eigenvector of $\mathcal{J}_2^2$ and $\mathcal{J}_{2z}$. Now the operators $\mathcal{J}_1^2, \mathcal{J}_2^2, \mathcal{J}_{1z}$ and $\mathcal{J}_{2z}$ commute with each other and the product functions

$$\psi(j_1, j_2, m_1, m_2) = \psi_1(j_1, m_1)\, \psi_2(j_2, m_2) \tag{11}$$

represent a set of simultaneous eigenvectors of J_1^2, J_2^2, J_{1z} and J_{2z}. Further, for given values of j_1 and j_2 there will be $(2j_1 + 1)$ possible values of m_1 and $(2j_2 + 1)$ possible values of m_2. Thus there will be $(2j_1 + 1)(2j_2 + 1)$ possible eigenvectors.

Now, the operators $\mathcal{J}_1^2, \mathcal{J}_2^2, \mathcal{J}^2$ and $\mathcal{J}_z$ also commute with each other (see Problem 10.1) and thus one can construct vectors $\phi(j_1, j_2, j, m)$ which are simultaneous eigenvectors of the operators $\mathcal{J}_1^2, \mathcal{J}_2^2, \mathcal{J}^2$ and $\mathcal{J}_z$ belonging to the eigenvalues $j_1(j_1 + 1), j_2(j_2 + 1), j(j + 1)$ and m respectively. In Sec. 10.2 we will show that the allowed values of j are

$$j_1 + j_2,\ j_1 + j_2 - 1, \dots |j_1 - j_2|$$

and since for each value of j there will be $(2j + 1)$ values of m, the total number of ϕ functions (for given values of j_1 and j_2) will be

$$\sum_{j=|j_1-j_2|}^{j=j_1+j_2} (2j + 1) = (2j_1 + 1)(2j_2 + 1) \tag{12}$$

which is the same as the number of ψ functions.

We can choose either the ψ functions or the ϕ functions as the base states and can represent each of the ψ functions as a linear combination of ϕ functions and conversely. Now the ψ functions as well as the ϕ functions form an orthonormal sets and if we normalize them then the transformation

$$\phi(j_1, j_2, j, m) = \sum_{m_1}\sum_{m_2} C(j_1, j_2; j, m, m_1, m_2)\, \psi(j_1, j_2, m_1, m_2) \tag{13}$$

is unitary and the coefficients

$$C(j_1, j_2; j, m, m_1, m_2) = \langle j_1, j_2, m_1, m_2 \mid j_1, j_2, j, m \rangle \tag{14}$$

are known as the Clebsch-Gordan coefficients. The coefficients play an extremely important role in spectroscopy and also in scattering theory.* The general formulae for calculating these coefficients are complicated. In Sec. 10.3 we will calculate these coefficients for $j_1 = j_n = \frac{1}{2}$ and give tables for calculation of these coefficients for $j_2 = \frac{1}{2}$ and $j_2 = 1$ (for arbitrary values of j_1). In Problem 10.3 we will calculate these coefficients for $j_1 = 1$ and $j_2 = \frac{1}{2}$. It can be easily seen that $\psi(j_1, j_2, m_1, m_2)$ are eigenfunctions of J_z belonging to the eigenvalue $(m_1 + m_2)$ but, in general, they are not eigenfunctions of J^2. In Sec. 10.4 we discuss the isospin and show how Clebsch-Gordan coefficients can be used in pion-nucleon systems.

10.2 The Possible Values of j

Let us first consider the case $j_1 = 1$ and $j_2 = \frac{1}{2}$; thus m_1 takes the values 1, 0 and -1 and m_2 takes the values $\frac{1}{2}, -\frac{1}{2}$. Consequently, there are six ψ functions

$$\begin{aligned} &\psi(1, \tfrac{1}{2}), \quad \psi(0, \tfrac{1}{2}), \quad \psi(-1, \tfrac{1}{2}) \\ &\psi(1, -\tfrac{1}{2}), \quad \psi(0, -\tfrac{1}{2}) \quad \text{and} \quad \psi(-1, -\tfrac{1}{2}) \end{aligned} \tag{15}$$

where we have omitted the values of j_1 and j_2. The numbers inside the parenthesis denote the values of m_1 and m_2. Clearly, the values of $m (= m_1 + m_2)$ are

$$\tfrac{3}{2}, \tfrac{1}{2}, -\tfrac{1}{2}, +\tfrac{1}{2}, -\tfrac{1}{2} \quad \text{and} \quad -\tfrac{3}{2}$$

The maximum value of m is $\frac{3}{2}$ and thus one of the j values must be $\frac{3}{2}$ which will give rise to four states with $m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$. The remaining two states must correspond to $j = \frac{1}{2}$ with $m = \frac{1}{2}$ and $-\frac{1}{2}$. Thus the allowed values of j are 3/2 and 1/2 and the corresponding φ vectors being

$$\begin{aligned} &\phi(\tfrac{3}{2}, \tfrac{3}{2}), \quad \phi(\tfrac{3}{2}, \tfrac{1}{2}), \quad \phi(\tfrac{3}{2}, -\tfrac{1}{2}), \\ &\phi(\tfrac{3}{2}, -\tfrac{3}{2}), \quad \phi(\tfrac{1}{2}, \tfrac{1}{2}) \quad \text{and} \quad \phi(\tfrac{1}{2}, -\tfrac{1}{2}) \end{aligned} \tag{16}$$

where the numbers inside the parenthesis are the values of j and m; once again we have omitted the values of j_1 and j_2. Now $\psi(1, \frac{1}{2}) = \varphi(\frac{3}{2}, \frac{3}{2})$ because these are the only functions which correspond to $m = \frac{3}{2}$. Further, since $\psi(0, \frac{1}{2})$ and $\psi(1, -\frac{1}{2})$ correspond to $m = \frac{1}{2}$, $\phi(\frac{3}{2}, \frac{1}{2})$ and $\phi(\frac{1}{2}, \frac{1}{2})$ should be linear combinations of $\psi(0, \frac{1}{2})$ and $\psi(1, -\frac{1}{2})$. Similarly $\phi(\frac{3}{2}, -\frac{1}{2})$ and $\phi(\frac{1}{2}, -\frac{1}{2})$ should be linear combinations of $\psi(0, -\frac{1}{2})$ and $\psi(-1, \frac{1}{2})$ and finally $\phi(\frac{3}{2}, -\frac{3}{2}) = \psi(-1, -\frac{1}{2})$.

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*Some of the uses of Clebsch-Gordan coefficients in spectroscopy problems are discussed in Chapters 11, 15 and 19. Applications in scattering theory can be found in Kogan and Gatsliky (1963), Cence (1969) and most of the texts in nuclear physics.

Let us next consider the general case and assume, without any loss of generality, that $j_1 \geqslant j_2$. The maximum values of m_1 and m_2 will be j_1 and j_2 and therefore the maximum value of j will be

$$j_{\max} = (m_1 + m_2)_{\max} = j_1 + j_2$$

and there will be only one ψ vector and only one φ vector which will correspond to $m = j_1 + j_2$ which should be equal. Thus

$$\phi(j_1, j_2, j_1 + j_2, j_1 + j_2) = \psi(j_1, j_2, j_1, j_2) \tag{17}$$

The next largest value of m will be $j_1 + j_2 - 1$ which will give rise to two ψ vectors

$$\psi(j_1, j_2 - 1) \quad \text{and} \quad \psi(j_1 - 1, j_2) \tag{18}$$

and two ϕ vectors

$$\phi(j_1 + j_2, j_1 + j_2 - 1) \quad \text{and} \quad \phi(j_1 + j_2 - 1, j_1 + j_2 - 1) \tag{19}$$

where we have omitted j_1, j_2 inside the brackets. The next value of m will be $j_1 + j_2 - 2$ which will give rise to three ψ vectors and three φ vectors. In general, for $m = j_1 + j_2 - k$, we will have the following $(k + 1)$ ψ vectors

$$\psi(j_1 - k, j_2); \quad \psi(j_1 - k + 1, j_2 - 1); \ldots \psi(j_1, j_2 - k) \tag{20}$$

and the following φ vectors

$$\phi(j_1 + j_2, j_1 + j_2 - k); \quad \phi(j_1 + j_2 - 1, j_1 + j_2 - k); \ldots \\ \phi(j_1 + j_2 - k, j_1 + j_2 - k) \tag{21}$$

Each ϕ vector can be expressed as a linear combination of the $(k + 1)$ ψ vectors, the constant coefficients being the Clebsch-Gordan coefficients. Now, since $j_1 \geqslant j_2$ the maximum value of k should be such that $j_2 - k$ equals $-j_2$ [see Eq. (20)] or $k_{\max} = 2j_2$ and therefore

$$j_{\min} = j_1 + j_2 - k_{\max} = j_1 - j_2 \tag{22}$$

Thus the allowed values of j are

$$j_1 + j_2, j_1 + j_2 - 1, \ldots j_1 - j_2 \tag{23}$$

10.3 Clebsch-Gordan Coefficients for $j_1 = j_2 = \frac{1}{2}$

For $j_1 = j_2 = \frac{1}{2}$, $m_1 = \pm \frac{1}{2}$ and $m_2 = \pm \frac{1}{2}$ giving four ψ functions

$$\psi(\tfrac{1}{2}, \tfrac{1}{2}),\ \psi(\tfrac{1}{2}, -\tfrac{1}{2}),\ \psi(-\tfrac{1}{2}, \tfrac{1}{2}) \quad \text{and} \quad \psi(-\tfrac{1}{2}, -\tfrac{1}{2})$$

The allowed values of j are 1 and 0 and hence the four φ functions are

$$\phi(1, 1),\ \phi(1, 0)\ \phi(1, -1) \quad \text{and} \quad \phi(0, 0)$$

Obviously

$$\phi(1, 1) = \psi(, \tfrac{1}{2}) \tag{24}$$

and

$$\phi(1, -1) = \psi(-\tfrac{1}{2}, -\tfrac{1}{2}) \tag{25}$$

Further

$$\phi(1, 0) = c_1\,\psi(\tfrac{1}{2}, -\tfrac{1}{2}) + c_2\,\psi(-\tfrac{1}{2}, \tfrac{1}{2}) \tag{26}$$

and

$$\phi(0, 0) = c_3\,\psi(\tfrac{1}{2}, -\tfrac{1}{2}) + c_4\,\psi(-\tfrac{1}{2}, \tfrac{1}{2}) \tag{27}$$

Now

$$J_-\,\phi(1, 1) = J_-\,\psi(\tfrac{1}{2}, \tfrac{1}{2}) = (J_1)_-\,\psi(\tfrac{1}{2}, \tfrac{1}{2}) + (J_2)_-\,\psi(\tfrac{1}{2}, \tfrac{1}{2})$$

or, using Eq. (31) of Chapter 9

$$\sqrt{2}\,\phi(1, 0) = \psi(\tfrac{1}{2}, -\tfrac{1}{2}) + \psi(-\tfrac{1}{2}, \tfrac{1}{2})$$

Thus

$$\phi(1, 0) = \frac{1}{\sqrt{2}}\left[\psi\left(\frac{1}{2}, -\frac{1}{2}\right) + \psi\left(-\frac{1}{2}, \frac{1}{2}\right)\right] \tag{28}$$

and since $\phi(0, 0)$ must be orthogonal to $\phi(1, 0)$ we must have [see also Problem 10.2(c)]

$$\phi(0, 0) = \frac{1}{\sqrt{2}}\left[\psi\left(\frac{1}{2}, -\frac{1}{2}\right) - \psi\left(-\frac{1}{2}, \frac{1}{2}\right)\right] \tag{29}$$

(within an arbitrary phase factor). It can be easily seen that by using ladder operators on $\phi(1, 0)$ or on $\phi(1, -1)$ we cannot get $\phi(0, 0)$ (see also Problem 10.2). We can thus write

$$\begin{pmatrix} \phi(1, 1) \\ \phi(1, 0) \\ \phi(1, -1) \\ \phi(0, 0) \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} \psi(\frac{1}{2}, \frac{1}{2}) \\ \psi(\frac{1}{2}, -\frac{1}{2}) \\ \psi(-\frac{1}{2}, \frac{1}{2}) \\ \psi(-\frac{1}{2}, -\frac{1}{2}) \end{pmatrix} \tag{30}$$

The matrix elements are the Clebsch-Gordan coefficients. Corresponding to $j = 0$ there is only one state $\phi(0, 0)$ which is therefore known as a *singlet* state; for $j = 1$ there are three states [$\phi(1, 1)$, $\phi(1, 0)$ and $\phi(1, -1)$ and therefore $j = 1$ is referred to as the *triplet* state. Notice that the singlet state is antisymmetric with respect to the interchange of m_1 and m_2 whereas the triplet state is symmetric (see also Sec. 15.6).

TABLE 10.1†

CLEBSCH-GORDAN COEFFICIENTS FOR $j_2 = \frac{1}{2}$; $\langle j_1 \frac{1}{2} m_1 m_2 | j_1 \frac{1}{2}\, jm \rangle$

$j =$	$m_2 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j_1 + \frac{1}{2}$	$\sqrt{\dfrac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\dfrac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$
$j_1 - \frac{1}{2}$	$-\sqrt{\dfrac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\dfrac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$

TABLE 10.2†

CLEBSCH-GORDAN COEFFICIENTS FOR $j_2 = 1$; $\langle j_1\, 1\, m_1 m_2 | j_1\, 1\, jm \rangle$

$j =$	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
$j_1 + 1$	$\sqrt{\dfrac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}}$	$\sqrt{\dfrac{(j_1-m+1)(j_1+m+1)}{(2j_1+1)(j_1+1)}}$	$\sqrt{\dfrac{(j_1-m)(j_1-m+1)}{(2j_1+1)(2j_1+2)}}$
j_1	$-\sqrt{\dfrac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}}$	$\dfrac{m}{\sqrt{j_1(j_1+1)}}$	$\sqrt{\dfrac{(j_1-m)(j_1+m+1)}{2j_1(j_1+1)}}$
$j_1 - 1$	$\sqrt{\dfrac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}}$	$\sqrt{\dfrac{(j_1-m)(j_1+m)}{j_1(2j_1+1)}}$	$\sqrt{\dfrac{(j_1+m+1)(j_1+m)}{2j(2j_1+1)}}$

†Tables adapted from Condon and Shortley (1951).

The Clebsch-Gordan coefficients for $j_2 = 1$ and $j_2 = \frac{1}{2}$ are tabulated in Tables 10.1 and 10.2. For $j_2 = \frac{1}{2}$, the possible values of j could be $j_1 + \frac{1}{2}$ and $j_1 - \frac{1}{2}$. As an example, using the top row of Table 10.1 we can write down

$$\phi\left(j_1 + \frac{1}{2}, m_j\right) = \left(\frac{j_1 + \frac{1}{2} + m_j}{2j_1 + 1}\right)^{1/2} \psi(m_j - \tfrac{1}{2}, \tfrac{1}{2}) + \left(\frac{j_1 + \frac{1}{2} - m_j}{2j_1 + 1}\right)^{1/2} \psi(m_j + \tfrac{1}{2}, -\tfrac{1}{2}) \tag{31}$$

where we have put a subscript j on m so that the notation is the same as used in Solution 9.12. Now, for an electron in a hydrogen-like atom

$$\psi\left(m_l, \frac{1}{2}\right) = R_{nl}(r)\; Y_{l,m_l}(\theta, \varphi) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{32}$$

which when used in Eq. (31) immediately gives Eq. (100) of Chapter 9.

10.4 The Concept of Isospin

In this section we briefly introduce the concept of isospin and mention the use of Clebsch-Gordan coefficients in the addition of isospin; such considerations are of great importance in high energy nuclear scattering studies.[*]

It is well known that except for their differences in charge, neutrons and protons have very similar properties. Thus neutron and proton can be thought of as eigenstates of the nucleon. Now a group of elementary particles can be thought of possessing isospin τ if there are $(2\tau + 1)$ particles possessing nearly identical properties except for their charge. Thus protons and neutrons can be thought of possessing isospin $\tau = \frac{1}{2}$ with $\tau_z = +\frac{1}{2}$ and $\tau_z = -\frac{1}{2}$ states corresponding to the proton and neutron respectively.[**] Similarly, π-mesons have an isospin of 1 since they occur in $2\tau + 1$ $(=3)$ forms as positively charged $\pi^+(\tau_z = 1)$, uncharged $\pi^0(\tau_z = 0)$ and negatively charged $\pi^-(\tau_z = -1)$ mesons. The charge of the nucleons or mesons is given by

$$Q = |q| [\tau_z + \tfrac{1}{2}B] \tag{33}$$

where B is known as the *baryon number* and has the value $+1$ for nucleons and 0 for mesons.

As an example, we consider the isospin of a system of two nucleons. Assuming that for isospin also we can add the angular momenta in a manner similar to that discussed in Secs. 10.2 and 10.3, we have four possible states

$$\phi(1, 1) = \psi(\tfrac{1}{2}, \tfrac{1}{2}) \tag{34}$$

$$\phi(1, 0) = \frac{1}{\sqrt{2}} [\psi(\tfrac{1}{2}, -\tfrac{1}{2}) + \psi(-\tfrac{1}{2}, \tfrac{1}{2})] \tag{35}$$

$$\phi(1, -1) = \psi(-\tfrac{1}{2}, -\tfrac{1}{2}) \tag{36}$$

$$\phi(0, 0) = \frac{1}{\sqrt{2}} [\psi(\tfrac{1}{2}, -\tfrac{1}{2}) - \psi(-\tfrac{1}{2}, \tfrac{1}{2})] \tag{37}$$

Obviously $\psi(\frac{1}{2}, \frac{1}{2})$ corresponds to 2 protons because $\tau_{1z} = \tau_{2z} = \frac{1}{2}$ and similarly $\phi(1, -1)$ corresponds to 2 neutrons; both $\phi(1, 0)$ and $\phi(0, 0)$ correspond to one proton and one neutron. However, $\phi(1, 0)$ is a symmetric function and $\phi(0, 0)$ is antisymmetric. Now, the ground state of deuteron is a mixture of $^3S_1$ and $^3D_1$ states (see, e.g., Fermi, 1950, p. 114), thus it is symmetric in co-ordinates. It corresponds to spin 1 and therefore it is also symmetric in the spins of the two nucleons. The gene-ralized Pauli principle (see, e.g., Sachs, 1953, Ch. 7) requires that the wave function should be an antisymmetric in isospin variables and hence the isospin state must be $\phi(0, 0)$.

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[*] For a nice discussion on isospin the reader is referred to the books by Sachs (1953), Bethe and Morrison (1956), etc. A good discussion on the analysis of high energy nuclear scattering experiments can be found in Cence (1959), Bethe and Morrison (1956), etc.

[**] One may see the analogy with the spin angular momentum where $s_z = +\frac{1}{2}$ and $-\frac{1}{2}$ correspond to the spin up and spin down states (see Sec. 9.3).

PROBLEMS

PROBLEM 10.1

Show that the operators $\mathcal{J}_1^2, \mathcal{J}_2^2, \mathcal{J}^2$ and $\mathcal{J}_z$ commute with each other. In particular show that whereas $\mathcal{J}^2$ does not commute with $\mathcal{J}_{1z}$ and $\mathcal{J}_{2z}$ but it does commute with $\mathcal{J}_z = \mathcal{J}_{1z} + \mathcal{J}_{2z}$.

PROBLEM 10.2

(*a*) In Sec. 10.3, we had operated $\phi(1, 1)$ by $\mathcal{J}_-$ and obtained the Clebsch-Gordan coefficients. Show that the same coefficients are obtained if we had operated $\phi(1, -1)$ by $\mathcal{J}_+$.

(*b*) Operate $\phi(1, 0)$ [see Eq. (28)] by $\mathcal{J}_-$ to obtain Eq. (25).

(*c*) Operate Eq. (27) by $\mathcal{J}_-$ or $\mathcal{J}_+$ to show that $C_3 = -C_4$.

PROBLEM 10.3

Calculate from first principles the Clebsch-Gordan coefficients for $j_1 = 1$ and $j_2 = \frac{1}{2}$ and show that the results are consistent with Table 10.1. Use the calculated coefficients to write the wave functions for the *p*-states of an electron $(l = 1, s = \frac{1}{2})$ for $j = \frac{3}{2} (m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2})$ and for $j = \frac{1}{2}$ $(m_j = \frac{1}{2}, -\frac{1}{2})$.

PROBLEM 10.4

For $j_2 = \frac{1}{2}$, starting with the relation

$$\phi(j = j_1 + \tfrac{1}{2}, m_j = j_1 + \tfrac{1}{2}) = \psi(j_1, \tfrac{1}{2}) \tag{38}$$

Calculate the Clebsch-Gordan coefficients and show that the results are consistent with Table 10.1.

PROBLEM 10.5

In the electron spin-orbit interaction problem $j_1 = l, j_2 = s = \frac{1}{2}$ and $j = l \pm \frac{1}{2}$ [see Eq. (23); the same result is also obtained in Problem 9.12]. Assuming that the system is in a state in which $\mathcal{J}_1^2, \mathcal{J}_2^2, \mathcal{J}^2$ and $\mathcal{J}_z$ are well defined show that

$$\langle s_z \rangle = \pm \frac{m_j \hbar}{(2l + 1)} \tag{39}$$

where the upper and lower signs correspond to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ respectively.

PROBLEM 10.6

For a state in which $\mathcal{J}_1^2, \mathcal{J}_2^2, \mathcal{J}_{1z}$ and $\mathcal{J}_{2z}$ have the well defined values $j_1(j_1 + 1)\hbar^2$, $j_2(j_2 + 1)\hbar^2$, $m_1\hbar$ and $m_2\hbar$ show that

$$\langle \mathcal{J}^2 \rangle = [j_1(j_1 + 1) + j_2(j_2 + 1) + m_1 m_2]\hbar^2 \tag{40}$$

PROBLEM 10.7

If $j_1(=1)$ and $j_2(=\frac{1}{2})$ represent the isospin of pions and nucleons (see Sec

10.4), then the total isospin of a pion nucleon system j, would be either $\frac{3}{2}$ or $\frac{1}{2}$. Show that

$$|\pi^+p\rangle = |j = \tfrac{3}{2}, j_z = \tfrac{3}{2}\rangle = |\tfrac{3}{2}, \tfrac{3}{2}\rangle \tag{41}$$

$$|\pi^+n\rangle = \sqrt{\tfrac{1}{3}}\, |\tfrac{3}{2}, \tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}\, |\tfrac{1}{2}, \tfrac{1}{2}\rangle \tag{42}$$

$$|\pi^0p\rangle = \sqrt{\tfrac{2}{3}}\, |\tfrac{3}{2}, \tfrac{1}{2}\rangle - \sqrt{\tfrac{1}{3}}\, |\tfrac{1}{2}, \tfrac{1}{2}\rangle \tag{43}$$

$$|\pi^0n\rangle = \sqrt{\tfrac{2}{3}}\, |\tfrac{3}{2}, -\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{3}}\, |\tfrac{1}{2}, -\tfrac{1}{2}\rangle \tag{44}$$

$$|\pi^-p\rangle = \sqrt{\tfrac{1}{3}}\, |\tfrac{3}{2}, -\tfrac{1}{2} -\rangle \sqrt{\tfrac{2}{3}}\, |\tfrac{1}{2}, -\tfrac{1}{2}\rangle \tag{45}$$

$$|\pi^-n\rangle = |\tfrac{3}{2}, -\tfrac{3}{2}\rangle \tag{46}$$

SOLUTIONS

SOLUTION 10.1

$$\mathcal{J}^2 = \mathcal{J}_1^2 + \mathcal{J}_2^2 + 2\,(\mathcal{J}_{1x}\mathcal{J}_{2x} + \mathcal{J}_{1y}\mathcal{J}_{2y} + \mathcal{J}_{1z}\mathcal{J}_{2z})$$

Since $\mathcal{J}_1^2$ and $\mathcal{J}_2^2$ commute with each other and also with $\mathcal{J}_{1x}, \mathcal{J}_{2x}, \mathcal{J}_{1y} \ldots$, etc. $[\mathcal{J}^2, \mathcal{J}_1^2] = [\mathcal{J}^2, \mathcal{J}_2^2] = 0$. Further,

$$[\mathcal{J}_1^2, \mathcal{J}_z] = [\mathcal{J}_1^2, \mathcal{J}_{1z}] + [\mathcal{J}_1^2, \mathcal{J}_{2z}] = 0$$

Similarly $[\mathcal{J}_2^2, \mathcal{J}_z] = 0$. However, $[\mathcal{J}^2, \mathcal{J}_{1z}] \neq 0$, indeed

$$\begin{aligned}[\mathcal{J}^2, \mathcal{J}_{1z}] &= [\mathcal{J}_1^2, \mathcal{J}_{1z}] + [\mathcal{J}_2^2, \mathcal{J}_{1z}] + 2\,(\mathcal{J}_{1x}\,[\mathcal{J}_{2x}, \mathcal{J}_{1z}] + [\mathcal{J}_{1x}, \mathcal{J}_{1z},]\,\mathcal{J}_{2x} \\ &\quad + \mathcal{J}_{1y}\,[\mathcal{J}_{2y}, \mathcal{J}_{1z}] + [\mathcal{J}_{1y}, \mathcal{J}_{1z}]\,\mathcal{J}_{2y} + \mathcal{J}_{1z}\,[\mathcal{J}_{2z}, \mathcal{J}_{1z}] + [\mathcal{J}_{1z}, \mathcal{J}_{1z}]\,\mathcal{J}_{2z}) \\ &= 2\,(-i\,\mathcal{J}_{1y}\mathcal{J}_{2x} + i\,\mathcal{J}_{1x}\mathcal{J}_{2y})\end{aligned} \tag{47}$$

Similarly $[\mathcal{J}^2, \mathcal{J}_{2z}] = 2\,(-i\,\mathcal{J}_{1x}\mathcal{J}_{2y} + i\,\mathcal{J}_{1y}\mathcal{J}_{2x})$ (48)

Thus $[\mathcal{J}^2, \mathcal{J}_z] = [\mathcal{J}^2, \mathcal{J}_{1z} + \mathcal{J}_{2z}] = 0$

SOLUTION 10.3

We follow a procedure similar to that used in Sec. 10.3. Now, $j_1 = 1$; $j_2 = \frac{1}{2}$; $m_1 = +1, 0, -1$; $m_2 = \pm\frac{1}{2}$; $j = \frac{3}{2}, \frac{1}{2}$ and

$$\phi(\tfrac{3}{2}, \tfrac{3}{2}) = \psi(1, \tfrac{1}{2}) \tag{49}$$

$$\phi(\tfrac{3}{2}, -\tfrac{3}{2}) = \psi(-1, -\tfrac{1}{2}) \tag{50}$$

Thus

$$\mathcal{J}_-\,\phi(\tfrac{3}{2}, \tfrac{3}{2}) = [(\mathcal{J}_1)_- + (\mathcal{J}_2)_-]\,\psi(1, \tfrac{1}{2})$$

If we use Eq. (31) of Chapter 9 we would get

$$\phi\left(\frac{3}{2},\frac{1}{2}\right)=\frac{1}{\sqrt{3}}\psi\left(1,-\frac{1}{2}\right)+\sqrt{\frac{2}{3}}\,\psi\left(0,\frac{1}{2}\right) \tag{51}$$

If we operate again by J_- (or operate Eq. (50) by J_+) we would get

$$\phi\left(\frac{3}{2},\frac{1}{2}\right)=\sqrt{\frac{2}{3}}\psi\left(0,-\frac{1}{2}\right)+\sqrt{\frac{1}{3}}\,\psi\left(-1,\frac{1}{2}\right) \tag{52}$$

Now $\varphi(\frac{1}{2},\frac{1}{2})$ has to be a linear combination of $\psi(1,-\frac{1}{2})$ and $\psi(0,\frac{1}{2})$ (because only these ψ functions give $m=\frac{1}{2}$), thus we may write

$$\phi(\tfrac{1}{2},\tfrac{1}{2})=c_1\,\psi(1,-\tfrac{1}{2})+c_2\,\psi(0,\tfrac{1}{2})$$

Since it has to be orthogonal to $\phi(\frac{3}{2},\frac{1}{2})$ we must have

$$\frac{c_1}{\sqrt{3}}+c_2\sqrt{\frac{2}{3}}=0$$

or

$$\phi\left(\frac{1}{2},\frac{1}{2}\right)=c_1\left[\psi\left(1,-\frac{1}{2}\right)-\frac{1}{\sqrt{2}}\psi\left(0,\frac{1}{2}\right)\right]$$

Using the normalization condition we get $c_1=\sqrt{\frac{2}{3}}$, giving

$$\phi(\tfrac{1}{2},\tfrac{1}{2})=\sqrt{\tfrac{2}{3}}\,\psi(1,-\tfrac{1}{2})-\sqrt{\tfrac{1}{3}}\,\psi(0,\tfrac{1}{2}) \tag{53}$$

Operating $\phi(\frac{1}{2},\frac{1}{2})$ by J_- we get

$$\phi\left(\frac{1}{2},-\frac{1}{2}\right)=\frac{1}{\sqrt{3}}\psi\left(0,-\frac{1}{2}\right)-\sqrt{\frac{2}{3}}\,\psi\left(-1,\frac{1}{2}\right) \tag{54}$$

Equations (49)–(54) give the Clebsch-Gordan coefficients. Notice that the ϕ functions automatically form an orthonormal set.

SOLUTION 10.5

Writing l for j_1, in Eq. (31) we obtain

$$\langle s_z\rangle_{j=l+\frac{1}{2}}=\left[\frac{l+\frac{1}{2}+m_j}{2l+1}\right]\left(\frac{1}{2}\hbar\right)+\left[\frac{l+\frac{1}{2}-m_j}{2l+1}\right]\left(-\frac{1}{2}\hbar\right)=\frac{m_j\hbar}{2l+1} \tag{55}$$

and similarly for $j=l-\frac{1}{2}$.

SOLUTION 10.7

$$|j=\tfrac{3}{2},j_z=\tfrac{3}{2}\rangle=|j_{1z}=1,j_{2z}=\tfrac{1}{2}\rangle=|\pi^+p\rangle \tag{56}$$

$$|j=\tfrac{3}{2},j_z=-\tfrac{3}{2}\rangle=|j_{1z}=-1,j_{2z}=-\tfrac{1}{2}\rangle=|\pi^-n\rangle \tag{57}$$

Now, using Eqs. (51) and (52)

$$|j = \tfrac{3}{2}, j_z = \tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}\,|j_{1z} = 1, j_{2z} = -\tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}\,|j_{1z} = 0, j_{2z} = \tfrac{1}{2}\rangle$$
$$= \sqrt{\tfrac{1}{3}}\,|\pi^+ n\rangle + \sqrt{\tfrac{2}{3}}\,|\pi^0 p\rangle. \tag{58}$$

and

$$|j = \tfrac{3}{2}, j_z = -\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\,|\pi^0 n\rangle + \sqrt{\tfrac{1}{3}}\,|\pi^- p\rangle, \text{ etc.} \tag{59}$$

Similarly we may use Eqs. (53) and (54). Simple algebra will then give Eqs. (42)–(45).

CHAPTER ELEVEN

Time Independent Perturbation Theory

11.1 Introduction

In Chapters 3, 4 and 5 we had obtained exact solutions of the Schrödinger equation for specific potential energy variations. However, for most problems in quantum mechanics, it is extremely difficult to obtain exact solutions of the Schrödinger equation and one has to resort to approximate methods. The three most important approximate methods are (i) the perturbation method, (ii) the variational method and (iii) the WKB method*; the perturbation method will be discussed in this chapter, the variational method will be discussed in Chapter 12 and the WKB method in Chapter 13. We may mention here that the variational method can give good estimate of the ground state energy by choosing an appropriate trial function; however, the method becomes quite cumbersome when one has to apply it to higher excited states. On the other hand, the WKB method gives an approximate but direct solution of the Schrödinger equation. The WKB method is applicable to potentials which are such that the Schrödinger equation is separable to a one-dimensional equation and when the potential is smoothly varying; if these conditions are satisfied, the method gives information about all the states of the problem.

The perturbation method, which is the subject matter of this chapter, is applicable when the Hamiltonian can be written as a sum of two parts

$$H = H_0 + H' \tag{1}$$

where the eigenvalues and eigenfunctions of H_0 are known and the effect of H' can be assumed to be small; H_0 is usually referred to as the unperturbed Hamiltonian and H' is known as the perturbation. We write the eigenvalue equation for the unperturbed Hamiltonian as

$$H_0\, u_n = E_n\, u_n \tag{2}$$

where E_n and u_n are *known* eigenvalues and orthonormal eigenfunctions of H_0 respectively. Our aim is to develop a perturbation method to solve the Schrödinger equation

$$H\psi_n = W_n\psi_n \tag{3}$$

and obtain approximate expressions for W_n and ψ_n. In Sec. 11.2 we will develop the perturbation theory for non-degenerate states which will be followed by considerations for degenerate states (Sec. 11.3). The theory that we will develop has been extensively applied to solve many problems in quantum mechanics; some of these applications have also been discussed in this chapter.

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*A few simple numerical methods for solving the Schrödinger equation are discussed in Chapter 17.

11.2 Non-degenerate Case

We introduce a parameter* g and write

$$H = H_0 + gH' \tag{4}$$

Next, we express ψ_n and W_n as power series** in g, i.e. we write

$$\psi_n = \psi_n^{(0)} + g\,\psi_n^{(1)} + g^2\,\psi_n^{(2)}\dots \tag{5}$$

$$W_n = W_n^{(0)} + g\,W_n^{(1)} + g^2\,W_n^{(2)} + \dots \tag{6}$$

where the superscripts 0, 1, 2, . . . refer to the zeroeth order, first order, second order perturbation and the parameter g is assumed to take a continuous range of values between zero and unity. In the final result we will set $g = 1$. We substitute the expansions given by Eqs. (5) and (6) in Eq. (3) to obtain

$$\begin{aligned}(H_0 + gH')\,(\psi_n^{(0)} + g\,\psi_n^{(1)} + g^2\,\psi_n^{(2)} + \dots)\\ = (W_n^{(0)} + gW_n^{(1)} + g^2W_n^{(2)} + \dots)\,(\psi_n^{(0)} + g\,\psi_n^{(1)} + g^2\psi_n^{(2)} + \dots)\end{aligned} \tag{7}$$

Since the above equation is supposed to be valid for all values of g lying between 0 and 1, the coefficients of equal powers of g on either side of the equation must be the same; i.e.,

$$H_0\,\psi_n^{(0)} = W_n^{(0)}\,\psi_n^{(0)} \tag{8}$$

$$H_0\,\psi_n^{(1)} + H'\,\psi_n^{(0)} = W_n^{(0)}\,\psi_n^{(1)} + W_n^{(1)}\,\psi_n^{(0)} \tag{9}$$

$$H_0\,\psi_n^{(2)} + H'\,\psi^{(1)} = W_n^{(0)}\,\psi_n^{(\ )} + W_n^{(1)}\,\psi_n^{(1)} + W_n^{(2)}\,\psi_n^{(0)} \tag{10}$$

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*This method is often used in mathematics. For Example, if we wish to solve the equation

$$u = a + \epsilon u^2 \tag{i}$$

where ϵ is a small number, we may write

$$u = u_0 + \epsilon\,u_1 + \epsilon^2 u_2 + \dots \tag{ii}$$

If we substitute this series in equation (i) above and equate powers of ϵ, we obtain $u_0 = a$, $u_1 = u_0^2 = a^2$; $u_2 = 2u_0u_1 = 2a^3$, etc. Thus

$$u = a + \epsilon a^2 + 2\epsilon^2 a^3 + \dots$$

In this particutar case, an exact solution of equation (i) can also be found

$$u = \frac{1}{2\epsilon}\left[\,1 - (4a\epsilon)^{\frac{1}{2}}\right] = a + \epsilon a^2 + 2\epsilon^2 a^3 + \dots$$

where we have chosen that root which makes $u \to a$ as $\epsilon \to 0$. Further the series will be convergent only when $4a\epsilon < 1$. For further details on perturbation techniques, see Bellman (1966).

**For example, if H' is proportional to the strength of the electric field $\mathcal{E}$ then $\psi_n^{(1)}$, $\psi_n^{(2)}$, $\psi_n^{(3)}$ . . . will be proportional to $\mathcal{E}$, $\mathcal{E}^2$, $\mathcal{E}^3$, . . . respectively; $\psi_n^{(0)}$ will be independent of $\mathcal{E}$. In some cases, such a power series may not be convergent [see, e.g. Eq. (37)]; indeed if it is an asymptotic series (see Appendix K), the first few terms may give fairly good results.

etc. Equation (8) tells us that $\psi_n^{(0)}$ and $W_n^{(0)}$ are the eigenfunctions and eigenvalues of the unperturbed Hamiltonian. Thus

$$\psi_n^{(0)} = u_n \tag{11}$$

and

$$W_n^{(0)} = E_n \tag{12}$$

We will be considering the effect of the perturbation H' on the nth state which will be assumed to be discrete and non-degenerate*; however, other states need neither be discrete nor be non-degenerate.

11.2.1 FIRST ORDER PERTURBATION

We assume that the eigenfunctions of the unperturbed Hamiltonian, H_0, form a complete set; thus we may express $\psi_n^{(1)}$ as a linear combination of the functions u_n

$$\psi_n^{(1)} = \sum_m a_m^{(1)} u_m \tag{13}$$

where the superscript (1) refers to the fact that we are considering first order perturbation. The summation appearing in the above equation actually represents a summation over the discrete states and integration over the continuum. If we substitute the above expansion in Eq. (9), we would obtain

$$H_0 \sum_m a_m^{(1)} u_m + H' \psi_n^{(0)} = W_n^{(0)} \psi_n^{(1)} + W_n^{(1)} \psi_n^{(0)} \tag{14}$$

or

$$\sum_m a_m^{(1)} E_m u_m + H' u_n = E_n \sum_m a_m^{(1)} u_m + W_n^{(1)} u_n \tag{15}$$

where we have used Eqs. (2) and (11). If we now multiply the above equation by u_k^* and integrate, we would get

$$\sum_m a_m^{(1)} E_m \delta_{km} + H'_{kn} = E_n \sum_m a_m^{(1)} \delta_{km} + W_n^{(1)} \delta_{kn}$$

or, carrying out the summations we get

$$a_k^{(1)} (E_n - E_k) + W_n^{(1)} \delta_{kn} = H'_{kn} \tag{16}$$

where

$$H'_{kn} \equiv \int u_k^* H' u_n \, d\tau = \langle k \,|\, H' \,|\, n \rangle \tag{17}$$

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*The corresponding theory for degenerate states is discussed in Sec. 11.3.

and we have used the orthonormality condition

$$\langle k \,|\, m \rangle = \int u_k^* u_m \, d\tau = \delta_{km}$$

For $k = n$, Eq. (16) gives

$$W_n^{(1)} = H'_{nn} = \int u_n^* H' u_n \, d\tau = \langle n \,|\, H' \,|\, n \rangle \tag{18}$$

which represents the first order perturbation to the energy. For $k \neq n$, Eq. (16) gives

$$a_k^{(1)} = \frac{H'_{kn}}{(E_n - E_k)}, \quad k \neq n \tag{19}$$

Notice that we have not been able to determine $a_n^{(1)}$. However, it can be easily seen from Eq. (9) that if we add an arbitrary multiple of u_n to $\psi_n^{(1)}$, the equation remains unaltered. Hence, without any loss of generality, we may assume

$$a_n^{(1)} = 0 \tag{20}$$

Such a choice implies

$$\int u^* \psi_n^{(1)} \, d\tau = 0 \tag{21}$$

11.2.2 SECOND ORDER PERTURBATION

We next expand $\psi_n^{(2)}$ as a linear combination of the eigenfunctions of H_0; thus, we write

$$\psi_n^{(2)} = \sum_m a_m^{(2)} u_m \tag{22}$$

where the superscripts refer to the fact that we are considering second order perturbation. Substituting the above expansion in Eq. (10) we get

$$H_0 \sum_m a_m^{(2)} u_m + H' \sum_m a_m^{(1)} u_m$$

$$= W_n^{(0)} \sum_m a_m^{(2)} u_m + W_n^{(1)} \sum_m a_m^{(1)} u_m + W_n^{(2)} u_n$$

Multiplying by u_k^* and integrating we obtain

$$\sum_m a_m^{(2)} E_m \delta_{km} + \sum_m a_m^{(1)} H'_{km}$$

$$= E_n \sum_m a_m^{(2)} \delta_{km} + H'_{nn} \sum_m a_m^{(1)} \delta_{km} + W_n^{(2)} \delta_{kn}$$

or

$$a_k^{(2)}\,(E_n - E_k) + W^{(2)}\,\delta_{kn} = \sum_m a_m^{(1)}\,H_{km} - a_k^{(1)}\,H'_{nn} \tag{23}$$

For $k = n$, we get

$$\begin{aligned} W_n^{(2)} &= \sum_m a_m^{(1)}\,H'_{nm} - a_n^{(1)}\,H'_{nn} \\ &= \sum_{\substack{m \\ m \neq n}}{}' a_m^{(1)}\,H'_{nm} \end{aligned}$$

where the prime over the summation indicates that we have omitted the term $m = n$. Thus, using Eq. (19), we get

$$W_n^{(2)} = \sum_m{}' \frac{|H'_{mn}|^2}{E_n - E_m} \tag{24}$$

where we have used the relation $H'_{nm} = (H'_{mn})^*$. The above equation gives the second order perturbation to the energy eigenvalue. Further, for $k \neq n$, Eq. (23) gives

$$a_k^{(2)} = \sum_m{}' \frac{H'_{km}\,H'_{mn}}{(E_n - E_k)\,(E_n - E_m)} - \frac{H'_{kn}\,H'_{nn}}{(E_n - E_k)^2} \tag{25}$$

Similarly, we may obtain $W_n^{(3)}$. The final result is

$$W_n = W_n^{(0)} + W_n^{(1)} + W_n^{(2)} + W_n^{(3)} + \dots \tag{26}$$

On substitution we obtain

$$\begin{aligned} W_n = E_n + H'_{nn} + \sum_m{}' \frac{|H'_{mn}|^2}{E_n - E_m} \\ + \left[\sum_m{}' \frac{|H'_{mn}|^2\,(H'_{mm} - H'_{nn})}{(E_n - E_m)^2}\right. \\ \left. + \frac{1}{3}\sum_m{}' \sum_{\substack{k \\ k \neq n \\ k \neq m}} \left\{\frac{1}{E_m - E_k} + \frac{1}{E_n - E_k}\right\} \frac{H'_{nk}H'_{km}H'_{mn} + H'_{nm}H'_{mk}H'_{kn}}{E_n - E_m}\right] \end{aligned} \tag{27}$$

11.2.3 TWO SIMPLE EXAMPLES

In order to illustrate the use of the perturbation theory to non-degenerate states we consider a perturbation of the form $\frac{1}{2}bx^2$ to the linear harmonic oscillator problem. Thus

$$H_0 = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \tag{28}$$

and

$$H' = \tfrac{1}{2} bx^2 \tag{29}$$

The eigenvalue and eigenfunctions of H_0 are well known (See Sec. 3.6.3)

$$H_0 u_n = E_n u_n \tag{30}$$

where

$$E_n = (n + \tfrac{1}{2})\hbar\omega; \quad n = 0, 1, 2, 3 \ldots \tag{31}$$

$$u_n = N_n H_n(\xi) \exp(-\tfrac{1}{2}\xi^2) \tag{32}$$

with

$$\omega = \sqrt{\frac{k}{\mu}}, \quad N_n = \left[\frac{\alpha}{\sqrt{\pi}\, 2^n\, n!}\right]^{1/2} \tag{33}$$

$$\xi = \alpha x, \qquad \alpha = \sqrt{\frac{\mu\omega}{\hbar}} = \left[\frac{k}{\mu\hbar^2}\right]^{1/4}$$

Notice that the exact solution can easily be obtained; all that we have to do is to replace k by $k + b$. Thus if we write

$$H\psi_n = W_n\psi_n \tag{34}$$

where

$$H = H_0 + H' \tag{35}$$

then

$$W_n = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k}{\mu}}\left[1 + \frac{b}{k}\right]^{1/2} \tag{36}$$

or

$$W_n = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k}{\mu}}\left[1 + \frac{1}{2}\frac{b}{k} - \frac{1}{8}\frac{b^2}{k^2} + \ldots\right] \tag{37}$$

the binomial expansion being valid when $b/k < 1$. If we compare Eq. (37) with Eq. (6), we obtain

$$W_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k}{\mu}} = E_n \tag{38}$$

$$W_n^{(1)} = \frac{1}{2}\left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k}{\mu}}\,\frac{b}{k} \tag{39}$$

$$W_n^{(2)} = -\frac{1}{8}\left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k}{\mu}}\,\frac{b^2}{k^2}, \text{ etc.} \tag{40}$$

where $W_n^{(0)}$ represents the unperturbed eigenvalue, and $W_n^{(1)}$ and $W^{(2)}$ represent the first and the second order perturbations respectively. Notice that $W_n^{(1)}$ is linear in b, $W_n^{(2)}$ is quadratic in b, etc. Further, the power series is convergent only ween $b/k < 1$.

Let us now employ perturbation theory to calculate $W_n^{(1)}$, $W_n^{(2)}$, etc. Now

$$W_n^{(1)} = \frac{1}{2} b \int_{-\infty}^{\infty} u_n^*(x)\, x^2\, u_n(x)\, dx = \frac{1}{2} b \langle n | x^2 | n \rangle$$

$$= \frac{1}{2}\left(n + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{\mu}}\, \frac{b}{k} \text{ (see footnote)} \tag{41}$$

which agrees with Eq. (39). In order to calculate $W_n^{(2)}$ we note that

$$H'_{mn} = \langle M | H' | n \rangle = \tfrac{1}{2} b \langle m | x^2 | n \rangle \tag{42}$$

is non zero only when* $m = n - 2$, $m = n$ or $m = n + 2$. Thus

$$W_n^{(2)} = \sum_m{}' \frac{|H'_{mn}|^2}{E_n - E_m}$$

$$= \frac{1}{2} b^2 \left[\frac{|\langle n-2 | x^2 | n \rangle|^2}{E_n - E_{n-2}} - \frac{|\langle n+2 | x^2 | n \rangle|^2}{E_{n+2} - E_n} \right]$$

$$= -\frac{1}{8} b^2 \frac{\hbar}{\mu^2 \omega^3} \left(n + \frac{1}{2} \right) \tag{43}$$

which agrees with Eq. (40).

Another simple example is to consider a linear harmonic oscillator of charge e perturbed by an electric field $\mathcal{E}$ in the $+x$ direction. Thus

$$H_0 = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \tfrac{1}{2} \mu \omega^2 x^2 \tag{44}$$

$$^*\langle m | x^2 | n \rangle = \frac{\hbar}{2\mu\omega} \Big[\langle m | \bar{a}\bar{a} | n \rangle + \langle m | \bar{a}a | n \rangle + \langle m | a\bar{a} | n \rangle + \langle m | aa | n \rangle \Big]$$

$$= \frac{\hbar}{2\mu\omega} \Big[\sqrt{(n+1)(n+2)}\, \delta_{m,\, n+2} + (2n+1)\delta_{mn} + \sqrt{n(n-1)}\, \delta_{m,\, n-2} \Big]$$

where we have used Eqs. (65), (67) and (68) of Chapter 8. Thus

$$\langle m | x^2 | n \rangle = \begin{cases} \dfrac{\hbar}{2\mu\omega} \sqrt{(n+1)(n+2)} & \text{for } m = n + 2 \\ \dfrac{\hbar}{2\mu\omega} (2n+1) & \text{for } m = n \\ \dfrac{\hbar}{2\mu\omega} \sqrt{n(n-1)} & \text{for } m = n - 2 \\ 0 & \text{otherwise} \end{cases}$$

and

$$H' = -e\mathcal{E}x \tag{45}$$

Now,

$$\langle m | H' | n \rangle = -e\mathcal{E} \langle m | x | n \rangle$$

is non zero only when* $m = n \pm 1$. Thus $W_n^{(1)} = 0$ and

$$W_n^{(2)} = {\sum_m}' \frac{|H'_{mn}|^2}{E_n - E_m} = e^2\mathcal{E}^2 \left[\frac{|\langle n-1 | x | n \rangle|^2}{E_n - E_{n-1}} - \frac{|\langle n+1 | x | n \rangle|^2}{E_{n+1} - E_n} \right]$$

$$= -\frac{e^2\mathcal{E}^2}{2\mu\omega^2}$$

In this case also we can find an exact solution of the problem by shifting the origin. This can easily be seen because

$$H = H_0 + H' = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}\mu\omega^2 x^2 - e\mathcal{E}x$$

$$= -\frac{\hbar^2}{2\mu}\frac{d^2}{d\zeta^2} + \frac{1}{2}\mu\omega^2\zeta^2 - \frac{e^2\mathcal{E}^2}{2\mu\omega^2}$$

where $\zeta = x - e\mathcal{E}/\mu\omega$. Thus the exact eigenvalue spectrum is

$$W_n = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{e^2\mathcal{E}^2}{2\mu\omega^2} \tag{46}$$

It may be noted that in this case the second order theory happens to give the exact results.

11.3 Perturbation Theory for Degenerate States

In the perturbation theory developed in Sec. 11.2. the zeroeth order wavefunction satisfies the equation

$$H_0\psi_n^{(0)} = W_n^{(0)}\psi_n^{(0)} \tag{47}$$

$$^*\langle m | x | n \rangle = \sqrt{\frac{\hbar}{2\mu\omega}}\langle m | \bar{a} + a | n \rangle$$

$$= \sqrt{\frac{\hbar}{2\mu\omega}}\left[\sqrt{n+1}\ \delta_{m,n+1} + \sqrt{n}\,\delta_{m,n-1}\right]$$

Or

$$\langle m | x | n \rangle = \begin{cases} \sqrt{\dfrac{\hbar}{2\mu\omega}}\sqrt{n+1} & \text{for } m = n+1 \\ \sqrt{\dfrac{\hbar}{2\mu\omega}}\sqrt{n} & \text{for } m = n-1 \\ 0 & \text{otherwise} \end{cases}$$

[see Eq. (8)]. This equation implies that $\psi_n^{(0)}$ is the eigenfunction corresponding to the unperturbed Hamiltonian. If we consider the perturbation to the nth state then we put

$$W_n^{(0)} = E_n \quad \text{and} \quad \psi_n^{(0)} = u_n \tag{48}$$

where u_n and E_n represent the eigenfunction and the energy eigenvalue for the nth state respectively. Now, for a degenerate state, any linear combination of the eigenfunctions is also a possible eigenfunction (see Sec. 3.3); consequently, $\psi_n^{(0)}$ cannot be completely specified by its unperturbed energy. Further, we notice from Eq. (16) that corresponding to a degenerate state if $E_k = E_n$ (but $k \neq n$) then H'_{kn} must be zero [otherwise $a_k^{(1)}$ will be infinite, see Eq. (19)]. Hence, we must choose* for $\psi_n^{(0)}$ such linear combinations of u_n so that $H'_{kn} = 0$ for $k \neq n$. Obviously, the choice of the linear combination will depend on the form of H'. We illustrate the procedure by considering the splitting of the first excited state of the H atom by an electric field**. The $n = 2$ state of the H atom is 4-fold degenerate. The eigenfunctions*** are (see Secs. 5.3 and 6.4).

$$\left.\begin{aligned}
u_1 &= R_{20}\, Y_{00} = \frac{1}{\sqrt{4\pi}}\, R_{20}(r); && (n = 2, l = 0, m = 0)\\
u_2 &= R_{21}\, Y_{10} = \sqrt{\frac{3}{4\pi}}\, R_{21}(r) \cos\theta; && (n = 2, l = 1, m = 0)\\
u_3 &= R_{21}\, Y_{11} = -\sqrt{\frac{3}{8\pi}}\, R_{21}(r) \sin\theta\, e^{i\varphi}; && (n = 2, l = 1, m = 1)\\
u_4 &= R_{21}\, Y_{1-1} = \sqrt{\frac{3}{8\pi}}\, R_{21}(r) \sin\theta\, e^{-i\varphi}; && (n = 2, l = 1, m = -1)
\end{aligned}\right\} \tag{49}$$

where

$$\left.\begin{aligned}
R_{20}(r) &= \frac{1}{\sqrt{2}}\, \frac{1}{a_0^{3/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}\\
&\text{and}\\
R_{21}(r) &= \frac{1}{2\sqrt{6}}\, \frac{1}{a_0^{3/2}}\, \frac{r}{a_0}\, e^{-r/2a_0}
\end{aligned}\right\} \tag{50}$$

---

*This also follows from the fact that in calculating the first order perturbation when we use the expansion

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \ldots$$

we must know precisely $\psi^{(0)}$ which represents the eigenfunction to which ψ will collapse when the perturbation is made to go to zero. However, for a degenerate state, we have no *apriori* knowledge which would allow us to predict as to which linear combination will ψ collapse to. Indeed, Eq. (16) tells us that we must choose such linear combinations so that $H'_{kn} = 0$ for $k \neq n$ (among the degenerate eigenfunctions).

**The spliting of spectral lines due to an electric field is known as Stark effect.

***It should be noted that we could have started with linear combinations of u_1, u_2, u_3 and u_4; however, the functions should form an orthonormal set.

The corresponding eigenvalue is

$$W_2^{(0)} = -\frac{\pi e^4}{8\hbar^2}$$

(The ground state wave function is denoted by u_0). Let the required linear combination be

$$\psi^{(0)} = c_1u_1 + \ldots + c_4u_4 \tag{51}$$

If we substitute this linear combination in the following equation [see Eq. (9)]

$$H_0\psi^{(1)} + H'\psi^{(0)} = W^{(0)}\psi^{(1)} + W^{(1)}\psi^{(0)}$$

we would obtain

$$H_0 \sum_m a_m^{(1)}\, u_m + H'[c_1u_1 + c_2u_2 + c_3u_3 + c_4u_4]$$

$$= W_2^{(0)} \sum_m a_m^{(1)}\, u_m + W_2^{(1)}\, [c_1u_1 + c_2u_2 + c_3u_3 + c_4u_4]$$

where we have assumed

$$\psi_2^{(1)} = \sum_m a_m^{(1)}\, u_m$$

Thus

$$\sum_m a_m^{(1)}\, E_m u_m + H'[c_1u_1 + \ldots + c_4u_4]$$

$$= W_2^{(0)} \sum_m a_m^{(1)}\, u_m + W_2^{(1)}\, [c_1u_1 + \ldots + c_4u_4] \tag{52}$$

Multiplying by u_1^* and integrating we obtain

$$a_1^{(1)}\, W_2^{(0)} + [c_1H'_{11} + c_2H'_{12} + c_3H'_{13} + c_4\, H'_{14}] = W_2^{(0)}\, a_1^{(1)} + W_2^{(1)}c_1$$

where

$$H'_{ij} = \int u_i^*\, H'\, u_j\, d\tau$$

Rearranging we obtain

$$c_1(H'_{11} - W_2^{(1)}) + c_2\, H'_{12} + c_3\, H_{13} + c_4\, H'_{14} = 0 \tag{53}$$

Similarly, if we multiply Eq. (52) by u_2^*, u_3^* and u_4^* and integrate, we would obtain respectively the following equations

$$c_1H'_{21} + c_2(H'_{22} - W_2^{(1)}) + c_3H'_{23} + c_4H'_{24} = 0 \tag{54}$$

$$c_1H'_{31} + c_2\, H'_{32} + c_3(H'_{33} - W_2^{(1)})\, c_4H'_{34} = 0 \tag{55}$$

$$c_1H'_{41} + c_2H'_{42} + c_3H'_{43} + c_4(H'_{44} - W_2^{(1)}) = 0 \tag{56}$$

Obvioulу, for a g-fold degenerate state, we will obtain a set of g equations. Now for nontrivial solutions

$$\begin{vmatrix} H'_{11}-W_2^{(1)} & H'_{12} & H'_{13} & H'_{14} \\ H'_{21} & H'_{22}-W_2^{(1)} & H'_{23} & H'_{24} \\ H'_{31} & H'_{32} & H'_{33}-W_2^{(1)} & H_{34} \\ H'_{41} & H'_{42} & H'_{43} & H'_{44}-W_2^{(1)} \end{vmatrix} = 0 \qquad (57)$$

which is known as the secular equation. In our present problem

$$H' = -e\mathcal{E}z = -e\mathcal{E}r\cos\theta \qquad (58)$$

($e < 0$). Thus

$$\begin{aligned} H'_{23} &= \int u_2^* H' u_3\, d\tau \\ &= \iiint \left[\sqrt{\frac{3}{4\pi}}\, R_{21}(r)\cos\theta\right]\left[-e\mathcal{E}r\cos\theta\right] \\ &\qquad\times\left[-\sqrt{\frac{3}{8\pi}}\, R_{21}(r)\sin\theta\, e^{i\varphi}\right] r^2\, dr\sin\theta\, d\theta\, d\varphi \\ &= 0 \end{aligned}$$

because $\int_0^{2\pi} e^{i\varphi}\, d\varphi = 0$. Due to the same reason the matrix elements H'_{32}, H'_{13}, H'_{31}, H'_{14}, H'_{41}, and H'_{32} would vanish. By carrying out the integration over θ, it can easily be shown that H'_{11}, H'_{22}, H'_{33}, H_{44} and H_{34} would vanish. The only non-vanishing* matrix elements would be H'_{12} and H'_{21}. Now

$$\begin{aligned} H'^{*}_{21} = H'_{12} &= \int u_1^* H' u_2\, d\tau \\ &= \frac{\sqrt{3}(-e\mathcal{E})}{4\pi}\int_0^\infty \frac{1}{\sqrt{2}}\,\frac{1}{2\sqrt{6}}\,\frac{1}{a_0^3}\,\frac{r^2}{a_0}\left(1-\frac{r}{2a_0}\right)e^{-r/a_0}\, r^2 dr \\ &\qquad \int_0^\pi \cos^2\theta\,\sin\theta\, d\theta \int_0^{2\pi} d\varphi \qquad (59) \\ &= 3e\mathcal{E}a_0 = -g \end{aligned}$$

---

*This could have been directly deduced from the following reasoning. Since all the wavefunctions have definite parities and since H' has odd parity

$$\int u_1^* H' u_1\, d\tau = \ldots = \int u_4^* H' u_4\, d\tau = 0$$

where $g = 3\,|e|\,\mathcal{E}a_0$. Thus the secular equation becomes

$$\begin{vmatrix} -W_2^{(1)} & -g & 0 & 0 \\ -g & -W_2^{(1)} & 0 & 0 \\ 0 & 0 & -W_2^{(1)} & 0 \\ 0 & 0 & 0 & -W_2^{(1)} \end{vmatrix} = 0 \tag{60}$$

The roots are

$$W_2^{(1)} = +g,\ -g,\ 0,\ 0$$

Now, if we substitute the values of the matrix elements, Eqs. (53)–(56) become

$$\begin{aligned} -c_1W_2^{(1)} - c_2g &= 0 \\ -c_1g - c_2W_2^{(1)} &= 0 \\ c_3W_2^{(1)} &= 0 \\ c_4W_2^{(1)} &= 0 \end{aligned}$$

Clearly for $W_2^{(1)} = g$, $c_1 = -c_2$, $c_3 = c_4 = 0$ and the required linear combination is

$$\phi_1 = \frac{1}{\sqrt{2}}(u_1 - u_2) \tag{61}$$

where the factor $1/\sqrt{2}$ is such that ϕ_1 is normalized. Similarly for $W_2^{(1)} = -g$, $c_1 = c_2$, $c_3 = c_4 = 0$ and the required linear combination is

$$\phi_2 = \frac{1}{\sqrt{2}}(u_1 + u_2) \tag{62}$$

For the root $W_2^{(1)} = 0$, $c_1 = c_2 = 0$ and c_3 and c_4 are indeterminate. Thus

$$\phi_3 \text{ and } \phi_4 = c_3u_3 + c_4u_4 \tag{63}$$

The splitting of the level is shown in Fig. 11.1. As can be seen the degeneracy is partially lifted.

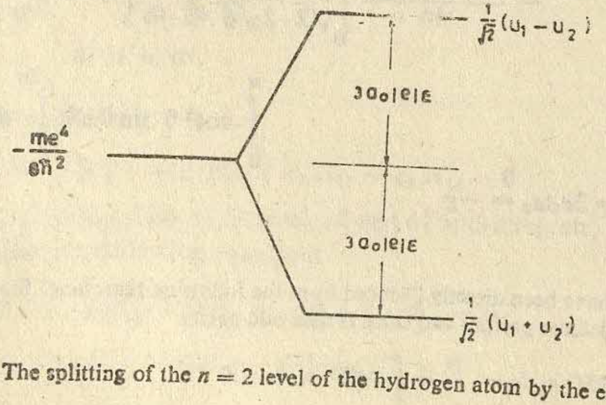

Fig. 11.1 The splitting of the $n = 2$ level of the hydrogen atom by the electric field.

The above theoretical predictions agree with the corresponding experimental values for electric field strengths less than about 10^4 volts/cm. For higher fields, the quadratic Stark effect has to be taken into account. Eventually, for field strengths greater than 10^5 volts/cm, autoionization occurs and Stark effect disappears.

11.4 Examples from Matrix Algebra

The use of the perturbation approach can be illustrated by considering examples from matrix algebra. We will discuss first the non-degenerate case and then the degenerate case.

CASE 1 : NON-DEGENERATE CASE

Let us consider the matrix*

$$H = \begin{pmatrix} 1+\epsilon & \epsilon \\ \epsilon & -1+\epsilon \end{pmatrix}$$

We write $H = H_0 + H'$, where

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad H' = \begin{pmatrix} \epsilon & \epsilon \\ \epsilon & \epsilon \end{pmatrix}$$

H_0 is assumed to represent the unperturbed matrix and H' represents the perturbation; $\epsilon \ll 1$. The eigenvalues of H_0 are $+1$ and -1; the corresponding eigenfunctions are

$$u_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad u_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Now, $$H'_{11} = (1 \;\; 0)\begin{pmatrix} \epsilon & \epsilon \\ \epsilon & \epsilon \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \epsilon$$

and $$H'_{22} = (0 \;\; 1)\begin{pmatrix} \epsilon & \epsilon \\ \epsilon & \epsilon \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \epsilon$$

Thus, in the first order perturbation theory, the eigenvalues are

$$1+\epsilon \quad \text{and} \quad -1+\epsilon$$

The exact eigenvalues of H are given by

$$\lambda = \epsilon \pm (1+\epsilon^2)^{1/2}$$

$$= 1+\epsilon+\tfrac{1}{2}\epsilon^2+\dots; \quad \text{and} \quad -1+\epsilon-\tfrac{1}{2}\epsilon^2+\dots$$

which agrees with the perturbation theory result.

---

*While considering examples from matrix algebra we must always have Hermitian matrices.

CASE 2 : DEGENERATE CASE

As before, we write $H = H_0 + H'$, where

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad H' = \begin{pmatrix} \epsilon & \epsilon \\ \epsilon & \epsilon \end{pmatrix}$$

Clearly the matrix H_0 has only one eigenvalue, viz., $+1$, which is two-fold degenerate. Further, any column matrix $\binom{\alpha}{\beta}$ is an eigenvector. We may choose

$$u_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad u_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Thus $\quad H'_{11} = (1 \quad 0)\begin{pmatrix} \epsilon & \epsilon \\ \epsilon & \epsilon \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \epsilon$

Similarly $H'_{22} = H'_{12} = H'_{21} = \epsilon$
Therefore, the secular determinant is

$$\begin{vmatrix} \epsilon - W & \epsilon \\ \epsilon & \epsilon - W \end{vmatrix} = 0$$

which gives

$$W = 0 \quad \text{and} \quad W = 2\epsilon$$

The degeneracy is lifted and according to first order perturbation theory the eigenvalues are

$$1 \text{ and } 1 + 2\epsilon$$

If we denote the eigenfunction by

$$\phi = c_1 u_1 + c_2 u_2$$

Then

$$c_1(\epsilon - W) + c_2\epsilon = 0$$

and

$$c_1\epsilon + c_2(\epsilon - W) = 0$$

For $\quad W = 0,\ c_1 = -c_2$ and

$$\phi_2 = \frac{1}{\sqrt{2}}(u_1 - u_2) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

For $W = 2\epsilon,\ c_1 = c_2$ and

$$\phi_2 = \frac{1}{\sqrt{2}}(u_1 + u_2) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Notice that

$$\phi^+ H'\phi_2 = \phi^+ H'\phi_1 = 0,$$

i.e., we have chosen such linear combinations in which H' is diagonal.

It is easy to show that if we try to directly determine the eigenvalues and eigenfunctions of H, we would obtain

$$(1+\epsilon-\lambda)^2=\epsilon^2 \text{ or}$$
$$\lambda = 1+\epsilon\pm\epsilon$$

Thus, it so happens that the first order perturbation theory gives the exact results.

11.5 Almost Degenerate Perturbation Theory

We next consider the case when the levels are 'almost degenerate', i.e., the corresponding energy eigenvalues are very nearly equal. For such a case the perturbation theory for non-degenerate states is strictly not valid because the corresponding expansion coefficient would become very large [see Eq. (19)]. We give here an approximate perturbation theory for a group of two levels which are almost degenerate. Let u_1 and u_2 represent the eigenfunctions of the two levels with energy eigenvalues E_1 and E_2; i.e.,

$$H_0\,u_{1,2}=E_{1,2}\,u_{1,2} \tag{64}$$

We write

$$\psi \simeq c_1u_1+c_2u_2 \tag{65}$$

and substitute in the eigenvalue equation

$$H\psi = W\psi$$

to obtain

$$c_1H_{11}+c_2H_{12}=Wc_1 \tag{66}$$

and

$$c_1H_{21}+c_2H_{22}=Wc_2 \tag{67}$$

where

$$H_{ij}=\int u_i^*\,Hu_j\,d\tau=\int u_i\,(H_0+H')\,u_j\,d\tau$$
$$=E_j\,\delta_{ij}+H'_{ij} \tag{68}$$

Equations (66) and (67) give us the secular determinant [cf. Eq. (57)]

$$\begin{vmatrix} H_{11}-W & H_{12} \\ H_{21} & H_{22}-W \end{vmatrix}=0 \tag{69}$$

which gives us

$$W_{1,2}=\tfrac{1}{2}\,[H_{11}+H_{22}]\pm\tfrac{1}{2}\,[(H_{11}-H_{22})^2+4\,|H_{12}|^2]^{1/2} \tag{70}$$

It is to be noted that when $E_1=E_2$ one obtains the result for degenerate states (see Sec. 11.3). On the other hand. when $|H_{11}-H_{22}|\gg|H_{12}|$, we get (by making a binomial expansion)

$$W_{1,2}\approx\tfrac{1}{2}\,[H_{11}+H_{22}]\pm\frac{1}{2}\left[\left(H_{11}-H_{22}\right)+\frac{1}{2}\,\frac{|H_{12}|^2}{H_{11}-H_{22}}\right] \tag{71}$$

Thus

$$W_1 = E_1 + H'_{11} + \frac{|H'_{12}|^2}{(E_1 + H'_{11}) - (E_2 + H'_{2})} \tag{72}$$

(and a similar expression for W_2) which agree with the result obtained by using non-degenerate perturbation theory to order g^2 because the term $(H'_{11} - H'_{22})$ in the denominator of the third term is itself of order g; g is the parameter introduced in Eq. (4). Thus Eq. (70) represents the general expression which in the appropriate limiting forms goes over to the expressions corresponding to non-degenerate and degenerate state perturbation theory.

11.6 Dalgarno's Method

If it becomes necessary to calculate the second order correction (viz., $W^{(2)}$) one has to evaluate the infinite sum given by Eq. (24) which, in general, is extremely difficult to carry out. However, in some cases it is possible to directly solve Eq. (9) and obtain an analytical expression for $\psi_n^{(1)}$ using which one can evaluate $W_n^{(2)}$ by using the expression

$$W_n^{(2)} = \int \psi_n^{(0)*} H' \psi_n^{(1)} \, d\tau - W_n^{(1)} \int \psi_n^{(0)*} \psi_n^{(1)} \, d\tau \tag{73}$$

(the above equation is obtained by multiplying Eq. 10 by $\psi_n^{(0)*}$ and integrating). This method is due to Dalgarno and is known as Dalgarno's method (see Dalgarno, 1961). We will illustrate its use by considering the Stark effect problem for the ground state of the hydrogen atom*. The perturbation is $H' = -e\mathcal{E}z = -e\mathcal{E}r\cos\theta$. Now $W_1^{(0)} = -\mu e^4/2\hbar^2$ and it is easy to show that $W_1^{(1)} = 0$. We rewrite Eq. (9)

$$H_0\psi_1^{(1)} + H'\psi_1^{(0)} = W_1^{(0)}\psi_1^{(1)} + W_1^{(1)}\psi_1^{(0)} \tag{74}$$

Thus

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{r} + \frac{\mu e^4}{2\hbar^2}\right]\psi_1^{(1)} = e\mathcal{E}r\cos\theta \, \frac{1}{\sqrt{4\pi}} \frac{2}{a_0^{3/2}} e^{-r/a_0} \tag{75}$$

where we have substituted the ground state wavefunction from Eq. (51) of Chapter 5. Since $\psi_1^{(1)}$ should go to zero as $\mathcal{E} \to 0$, we need find only the solution to the homogeneous part of the equation. We assume

$$\psi_1^{(1)} = R(r)\cos\theta \tag{76}$$

Thus

$$\nabla^2\psi_1^{(1)} = \left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2}{r^2}R(r)\right]\cos\theta \tag{77}$$

---

*Epstein has given another method for calculating the Stark effect problem in hydrogen atom. The method has been discussed in Pauling and Wilson (1935), p. 195.

or

$$\begin{aligned}\Bigg[-\frac{1}{2}\left\{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2}{r^2}R(r)\right\}\\ -\frac{1}{r}+\frac{1}{2}\Bigg]R(r)=\frac{C}{\sqrt{\pi}}e^{-r}\end{aligned} \tag{78}$$

where we have used the atomic system of units ($\hbar = 1$, $\mu = 1$, $e = 1$) and

$$C = \frac{\hbar^4}{\mu^2 e^5}\,\mathcal{E} \tag{79}$$

Let us introduce a function $F(r)$ such that

$$R(r) = r\,F(r)\,e^{-r} \tag{80}$$

On substitution in Eq. (78), we obtain

$$r\frac{d^2F}{dr^2} + (4 - 2r)\frac{dF}{dr} - 2\,F(r) = -\frac{2Cr}{\sqrt{\pi}} \tag{81}$$

We are interested in determining the inhomogeneous part of the solution. We find that $F(r) = a + br$ satisfies Eq. (81) provided we choose $a = 2b = c/\sqrt{\pi}$. Thus we obtain

$$R(r) = r\frac{C}{\sqrt{\pi}}\left(1 + \frac{1}{2}r\right)e^{-r}$$

and therefore

$$\psi_1^{(1)} = Cr\left(1 + \frac{1}{2}r\right)\frac{1}{\sqrt{\pi}}e^{-r}\cos\theta \tag{82}$$

Substituting in Eq. (73) and carrying out the integration we get

$$\begin{aligned}W_1^{(2)} &= -\tfrac{9}{4}c^2 \text{ atomic units}\\ &= -\frac{9}{4}\left(\frac{\hbar^4}{\mu^2 e^5}\mathcal{E}\right)^2\frac{\mu e^4}{\hbar^2} = -\frac{9}{4}\,a_0^3\,\mathcal{E}^2\end{aligned} \tag{83}$$

where $a_0 = \hbar^2/\mu e^2$ is the Bohr radius. Thus we may write

$$W_1 = W_1^{(0)} - \tfrac{9}{4}\,a_0^3\,\mathcal{E}^2 \tag{84}$$

Thus the polarizability[*] for the normal hydrogen atom is given by

$$\alpha = \tfrac{9}{2}\,a_0^3 = 0.677 \times 10^{-24}\ \text{cm}^3 \tag{85}$$

It can be shown that[**] $W_1^{(3)} = W_1^{(5)} = \ldots = 0$ and

$$\psi_1^{(2)}(r) = \left[\frac{31}{8} - \frac{7}{16}r^2 - \frac{r^3}{24} - \frac{1}{16}(15 + 10r + 2r^2)\right]C^2 \tag{86}$$

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[*] For details on polarizability one may refer to Pauling and Wilson (1935) Sec. 29e and 49f; Karplus and Porter (1970) Sec. 5.3.

[**] See, for example, Dalgarno (1961).

Further

$$W_1^{(4)} = -\frac{3555}{64} C^4 \tag{87}$$

PROBLEMS

PROBLEM 11.1

Consider an electron inside an infinitely deep one dimensional potential well

$$\begin{aligned} V(x) &= 0 \quad \text{for} \quad 0 < x < L \\ &= \infty \quad \text{for} \quad x < 0 \quad \text{and} \quad x > L \end{aligned}$$

(see Sec. 3.6.1). Assuming a perturbation of the form $H' = -e\mathcal{E}x$ show that in the first order perturbation theory each level gets shifted by $-e\mathcal{E}L/2$. Further, show that for the ground state ($n = 1$)

$$\psi^{(1)}(n = 1) = c_2\,\psi^{(0)}(n = 2) + c_3\,\psi^{(0)}(n = 3) + \ldots$$

where

$$c_2 = \frac{32}{27\pi^4}\left(\frac{\mu a^2}{\hbar^2}\right)(-e\mathcal{E}L), \text{ etc.}$$

PROBLEM 11.2

Consider the one dimensional harmonic oscillator problem (see Sec. 3.6.3). Assuming a perturbation $H' = \beta x^4$ show that

$$W_n^{(1)} = \frac{3\beta}{2(\mu\omega/\hbar)}\left(n^2 + n + \frac{1}{2}\right) \tag{88}$$

PROBLEM 11.3

Let the matrix

$$P = \begin{pmatrix} 1 & \epsilon \\ \epsilon & 3 \end{pmatrix}$$

be written in the form

$$P = P_0 + P'$$

where

$$P_0 = \begin{pmatrix} 1 & 0 \\ 0 & 3 \end{pmatrix} \quad \text{and} \quad P' = \begin{pmatrix} 0 & \epsilon \\ \epsilon & 0 \end{pmatrix}$$

Consider P' as the perturbation and use second order perturbation theory to calculate the eigenvalue of P. Compare the results with the ones obtained by diagonalizing the matrix P.

PROBLEM 11.4

Let the matrix

$$P = \begin{pmatrix} 1 & \epsilon & 0 \\ \epsilon & 1 & 0 \\ 0 & 0 & 2+\epsilon \end{pmatrix}$$

be written in the form $P = P_0 + P'$ where

$$P_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad \text{and} \quad P' = \begin{pmatrix} 0 & \epsilon & 0 \\ \epsilon & 0 & 0 \\ 0 & 0 & \epsilon \end{pmatrix}$$

Consider P' as the perturbation and use degenerate state perturbation theory to calculate the eigenvalues of P.

PROBLEM 11.5

Consider a particle in an infinitely deep potential well inside a cube of dimension L (see Problem 5.2). Consider a perturbation H' of the form

$$H' = kx^2$$

Apply first order perturbation theory to the first excited state which is 3-fold degenerate. Is the degeneracy completely lifted?

PROBLEM 11.6

Consider a Hamiltonian of the form

$$H = H_0 + H'$$

where

$$H_0 = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) + \frac{1}{2}k(x_1^2 + x_2^2)$$

and

$$H' = \lambda\, x_1 x_2$$

The above Hamiltonian represents two identical oscillators (along the same axis) with an interaction between the two. Treat H' as a perturbation and calculate the first order shift in the energy level of the first excited state. This problem can also be solved exactly. Obtain the exact solution and compare with the result obtained by using perturbation theory.

PROBLEM 11.7

The Hamiltonian H_0 for a two dimensional oscillator can be written in the form

$$H_0 = \frac{1}{2\mu}(p_x^2 + p_y^2) + \frac{1}{2}k(x^2 + y^2)$$

Consider a perturbation

$$H' = \tfrac{1}{2}k\epsilon xy\,(x^2 + y^2)$$

where ϵ is small. The eigenvalue equation for H_0 can easily be solved; the eigenvalues are simply $(n + m + 1)\hbar\omega$

$$H_0\, u_{n,m} = (n + m + 1)\,\hbar\omega\, u_{n,m};$$

with

$$u_{n,m} = N_n H_n(\xi)\, e^{-1/2\xi^2} N_m H_m(\eta)\, e^{-1/2\eta^2}$$

$$\xi = \alpha x, \quad \eta = \alpha y$$

(see Sec. 3.6.3). Show that for $\epsilon \neq 0$, in the first order perturbation theory, the ground state is not shifted and the 2-fold degenerate first excited state splits whose energies are given by

$$\left(2 \pm \frac{3}{4} \frac{\epsilon\hbar}{\sqrt{\mu k}}\right) \hbar\omega;$$

the corresponding eigenfunctions being

$$\frac{1}{\sqrt{2}} (u_{0,1} \pm u_{1,0})$$

PROBLEM 11.8

Using first order perturbation theory calculate the ground state energy of a helium-like atom; assume the interaction between the two electrons to represent the perturbation. Show that the first ionization potential for a single electron is given by

$$\left(\frac{1}{2} Z^2 - \frac{5}{8} Z\right) \frac{\mu e^4}{2\hbar^2}$$

You will have to assume the nucleus to be infinitely heavy—why? (see Solution 15.1 and Problem 15.6)

PROBLEM 11.9

While solving the Schrödinger equation for a hydrogen-like atom one assumes the nucleus to be a point charge. Using first order perturbation theory calculate the effect of the finite size of the nucleus assuming the nucleus to be a sphere of radius R_N with its charge uniformly distributed throughout its volume. (The effect of the finite size of the nucleus is usually referred to as volume effect and is important while considering isotope shift).

PROBLEM 11.10

The previous problem has an important application in muonic atom* which consists of a μ-meson and a nucleus ($m_\mu \simeq 207\, m_e$). First show that the Bohr radius for the muonic atom is comparable to the nuclear radius for $Z \approx 45$; thus for $Z \gtrsim 45$ the muon orbit may be inside the nucleus. Assuming the Coulomb potential to be a perturbation, calculate the energy levels of the muonic atom.

PROBLEM 11.11

According to the special theory of relativity, the relation between the energy and momentum for a free particle is

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*Muonic atoms may be formed when a muon slows down through matter. Such atoms have been obtained for $Z = 1$ to heavy elements like uranium.

$$E^2 = c^2p^2 + m^2c^4 \tag{89}$$

where m represents the rest mass of the particle and c the speed of light in free space. In the presence of the potential $V(r)$, Eq. 89 modifies to*

$$[E - V(r)^2] = c^2p^2 + m^2c^4 \tag{90}$$

If we replace $\mathbf{p}$ by $-i\hbar\nabla$ we obtain Schrödinger's relativistic equation

$$[-\hbar^2c^2\nabla^2 + m^2c^4]\,\psi = [E - V(r)]^2\,\psi \tag{91}$$

If we write $E = E' + mc^2$, the above equation can be written as

$$(H_0 + H')\,\psi = E'\psi \tag{92}$$

where

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \tag{93}$$

and

$$H' = -\frac{[E' - V(r)]^2}{2mc^2} \tag{94}$$

Without H' we have Schrödinger's non-relativistic equation; treat H' as perturbation and calculate its effect on the energy levels of hydrogen like atoms.

PROBLEM 11.12

In a hydrogen-like atom the spin orbit interaction is of the form (see Secs. 18.5 and 23.8)

$$H' = \frac{Ze^2}{2m^2c^2}\,\frac{1}{r^3}\,\mathbf{L}\cdot\mathbf{s} \tag{95}$$

Since $2\,\mathbf{L}\cdot\mathbf{s} = J^2 - L^2 - s^2$, choose a representation in which J^2, L^2 and s^2 are well defined and calculate the spin orbit correction. Incorporate also the relativity correction of Problem 11.11 to calculate the splitting of the $n = 2$ state. Show that for the $n = 3$ state the $S_{1/2}$ level coincides with the $P_{1/2}$ level and is separated from the $D_{3/2}$ level (which coincides with $P_{3/2}$ level) by 0.109 cm^{-1}; further the $D_{5/2}$ level is separated from the $D_{3/2}$ level by 0.036 cm^{-1}.

---

*Indeed in the presence of electromagnetic potentials, we have (see Sec. 18.2)

$$(E - Q\phi)^2 = c^2\left(\mathbf{p} - \frac{Q}{c}\,\mathbf{A}\right)^2 + mc^2$$

where Q is the charge of the particle, ϕ and $\mathbf{A}$ are the scalar and vector potentials.

PROBLEM 11.13

A plane rotator is defined by the Hamiltonian $H = M_z^2/2I$ where I is the moment of inertia and M_z is the operator of the component of angular momentum along the axis of rotation z. Replace M_z by $-i\hbar\,\partial/\partial\varphi$ and find the eigenvalues and normalized eigenfunctions of H. (You will only have to assume that the wavefunctions should be single valued.) If the rotator be perturbed by a constant field in its plane, in which its potential energy is $\mathcal{E}\cos\varphi$, show that to the order $\mathcal{E}^2$, the displacement of the level E_m is

$$\frac{\mathcal{E}^2 I}{\hbar^2(4m^2-1)}$$

PROBLEM 11.14

A particle moves in a potential that is central except for a small non-central perturbation

$$F(r)\,(3\cos^2\theta - 1)$$

Show that in first order perturbation theory, the energies of the s states of the system are unaffected and that the three p states ($l = 1$; $m = 1, 0, -1$) are respectively purturbed by $\frac{1}{2}A$, A and $-\frac{1}{2}A$ where A is determined from the form of the central potential and of $F(r)$.

[*Hint*: The unperturbed eigenfunctions of the p states are of the form $R(r)\,Y_{1,1}(\theta,\varphi)$; $R(r)\,Y_{1,0}(\theta,\varphi)$ and $R(r)\,Y_{1,-1}(\theta,\varphi)$].

PROBLEM 11.15

Consider the interaction between two hydrogen atoms in their ground state (this kind of interaction is known as van der Waal's interaction). Let A and B denote the positions of the nuclei of the two atoms; these nuclei are assumed to be fixed in space and separated by a distance R—see Fig. 11.2. Show that the Hamiltonian can be written in the form

$$H = H_0 + H' \tag{96}$$

where

$$H_0 = -\frac{\hbar^2}{2\mu}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_1} - \frac{e^2}{r_2} \tag{97}$$

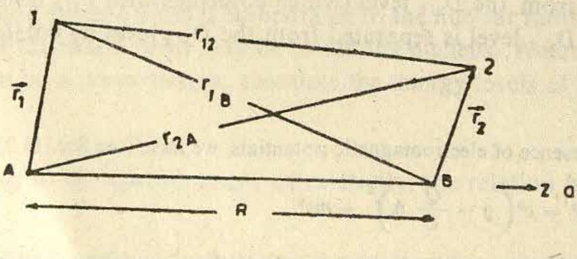

Fig. 11.2 The hydrogen molecule; A and B denote the positions of the two nuclei.

and

$$H' \approx \frac{e^2}{R}(x_1x_2 + y_1y_2 - 2\,z_1z_2) \tag{98}$$

x_1, x_2, etc. represent the x-coordinates of the electrons 1 and 2 with respect to the nuclei A and B respectively. Use perturbation theory to calculate the effect of H'. (The variational analysis of the hydrogen molecule and the hydrogen molecule ion is discussed in Sec. 12.7, Problems 12.4 and 12.5.)

SOLUTIONS

SOLUTION 11.5

If we refer to the solution to Problem 5.2. Then the energy eigenvalue corresponding to the first excited state is given by

$$W_1^{(0)} = \frac{6\pi^2\hbar^2}{2\mu L^2}$$

The state is 3-fold degenerate; the wave functions are

$$u_1 = \sqrt{\frac{8}{L^3}}\sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{\pi z}{L}\;[n_x = 2, n_y = 1, n_z = 1]$$

$$u_2 = \sqrt{\frac{8}{L^3}}\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L}\sin\frac{\pi z}{L}\;[n_x = 1, n_y = 2, n_z = 1]$$

$$u_3 = \sqrt{\frac{8}{L^3}}\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{2\pi z}{L}\;[n_x = 1, n_y = 1, n_z = 2]$$

Now

$$H'_{ij} = \int u_i^* H' u_j\,d\tau = k\iiint u_i^*\,x^2\,u_j\,dx\,dy\,dz$$

Simple integrations show that

$$H'_{ij} = 0 \quad \text{for} \quad i \neq j$$

Thus we already have a representation in which H' is diagonal. Further

$$H'_{11} = kL^2\left(\frac{1}{3} - \frac{1}{8\pi^2}\right) = g_1 \text{ (say)}$$

and

$$H'_{22} = H'_{33} = kL^2\left(\frac{1}{3} - \frac{1}{2\pi^2}\right) = g_2 \text{ (say)}$$

Hence the secular determinant is

$$\begin{vmatrix} g_1 - W_1^{(1)} & 0 & 0 \\ 0 & g_2 - W_1^{(1)} & 0 \\ 0 & 0 & g_2 - W_1^{(1)} \end{vmatrix} = 0$$

The roots are g_1, g_2, g_2; the degeneracy is partially lifted and the perturbed energy levels are

$$W_1^{(0)} + g_1, \quad W_1^{(0)} + g_2 \quad \text{and} \quad W_1^{(0)} + g_2.$$

SOLUTION 11.6

The normalized eigenfunctions of H_0 are

$$\psi^{(0)}_{n_1, n_2} = N\, H_{n_1}(\xi_1)\, H_{n_2}(\xi_2) \exp\left[-\tfrac{1}{2}(\xi_1^2 + \xi_2^2)\right]; \quad n_1, n_2 = 0, 1, 2 \ldots$$

where

$$\xi_1 = \alpha x_1, \quad \xi_2 = \alpha x_2, \quad \alpha = \left[\frac{\mu k}{\hbar}\right]^{1/4}$$

$$N = \frac{\alpha}{\sqrt{\pi}}\left[\frac{1}{2^{n_1} n_1!}\,\frac{1}{2^{n_2} n_2!}\right]^{1/2}$$

The corresponding eigenvalues are

$$W^{(0)}_{n_1, n_2} = (n_1 + n_2 + 1)\,\hbar\omega$$

The first excited state is two-fold degenerate ($n_1 = 0$, $n_2 = 1$ and $n_1 = 1$, $n_2 = 0$) the corresponding eigenvalue being $2\hbar\omega$. If we write $u_1 = \psi^{(0)}_{0,1}$, $u_2 = \psi^{(0)}_{1,0}$ and

$$H'_{ij} = \iint u_i\, H'\, u_j\, dx_1\, dx_2, \quad i, j = 1,2$$

then $\quad H'_{11} = H'_{22} = 0$ and

$$H'_{12} = \iint\limits_{-,\infty}^{\infty} u_1^* \,\lambda\, \frac{\xi_1 \xi_2}{\alpha^2}\, u_2\, \frac{d\xi_1 d\xi_2}{\alpha^2}$$

$$= \left(\frac{\alpha}{\sqrt{\pi}}\right)^2 \frac{1}{2}\,\frac{\lambda}{\alpha^4} \int_{-\infty}^{\infty} 2\xi_1^2\, e^{-\xi_1^2}\, d\xi_1 \int_{-\infty}^{\infty} 2\xi_2^2\, e^{-\xi_2^2}\, d\xi_2$$

$$= \frac{\lambda}{2\alpha^2} = \frac{\lambda}{2k}\,\hbar\omega = H'_{21}$$

On solving the secular equation, we obtain

$$W^{(1)} = \pm\, \frac{\lambda}{2k}\,\hbar\omega$$

the corresponding eigenfunctions being

$$\frac{1}{\sqrt{2}}(u_1 \pm u_2) = \frac{1}{\sqrt{2}}\left(\psi^{(0)}_{0,1} \pm \psi^{(0)}_{1,0}\right)$$

The exact eigenvalues of H can be determined if we introduce the new variables

$$\eta_1 = \frac{x_1 + x_2}{\sqrt{2}} \quad \text{and} \quad \eta_2 = \frac{x_1 - x_2}{\sqrt{2}}$$

Thus

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial\eta_1^2} + \frac{\partial^2}{\partial\eta_2^2}\right) + \frac{1}{2}(k+\lambda)\eta_1^2 + \frac{1}{2}(k-\lambda)\eta_2^2 .$$

the exact energy levels of which are given by (see Problem 5.5)

$$\left(n_1 + \frac{1}{2}\right)\hbar\sqrt{\frac{k+\lambda}{\mu}} + \left(n_2 + \frac{1}{2}\right)\hbar\sqrt{\frac{k-\lambda}{\mu}}\;;\quad n_1, n_2 = 0, 1, 2 \ldots$$

If we make a binomial expansion of the square root in powers of λ/k then the first order terms will be the same as obtained from the perturbation theory.

SOLUTION 11.9

The charge density inside the nucleus is

$$\frac{Z|e|}{\frac{4\pi}{3}R_N^3}$$

Thus the force acting on the electron will be given by

$$\left.\begin{aligned} F(r) &= -\frac{Ze^2}{\frac{4\pi}{3}R_N^3}\,\frac{4\pi}{3}r^3\,\frac{1}{r^2} && \text{for } 0 \leqslant r \leqslant R_N \\ &= -\frac{Ze^2}{r^2} && \text{for } \quad r \geqslant R_N \end{aligned}\right\} \tag{99}$$

Since $F(r) = -\dfrac{\partial V}{\partial r}$, we obtain (see Fig. 11.3)

$$\left.\begin{aligned} V(r) &= -\frac{Ze^2}{R_N}\left(\frac{3}{2} - \frac{1}{2}\frac{r^2}{R_N^2}\right) && \text{for } 0 \leqslant r \leqslant R_N \\ &= -\frac{Ze^2}{r} && \text{for } r \geqslant R_N \end{aligned}\right\} \tag{100}$$

where the zero of the potential energy has been assumed at $r = \infty$ and use has been made of the fact that $V(r)$ is continuous at $r = R_N$. The perturbation is therefore given by

$$\begin{aligned} H' &= -\frac{Ze^2}{R_N}\left(\frac{3}{2} - \frac{1}{2}\frac{r^2}{R_N^2}\right) + \frac{Ze^2}{r} && \text{for } 0 \leqslant r \leqslant R_N \\ &= 0 && \text{for } r \geqslant R_N \end{aligned}$$

Consequently

$$W_n^{(1)} = \int_0^{R_N} r^2\,dr \int_0^{\pi} \sin\theta\,d\theta \int_0^{2\pi} d\varphi\;[\psi_n^{(0)}]^*\,H'\,\psi_n^{(0)}$$

Since the radius of the nucleus is usually much smaller than the Bohr radius, we may assume the wavefunction to remain constant over the region of integration;

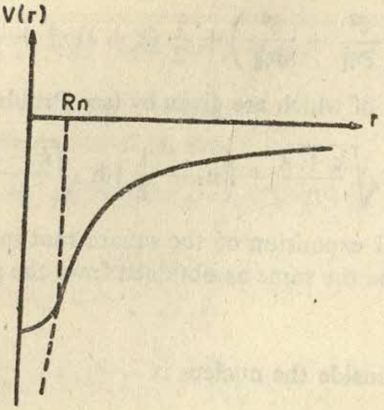

Fig. 11.3 The solid curve shows the variation of $V(r)$ (as given by Eq. 100) when the effect of the finite size of the nucleus has been taken into account. The dashed curve in the region $r < R_N$ is the extension of the $1/r$ variation.

thus we may replace $\psi_n^{(0)}$ by its value at $r = 0$. Consequently

$$W_n^{(1)} \simeq [R_{nl}(0)]^2 \int_0^{R_N} H' r^2\, dr \iint |Y_{lm}(\theta, \varphi)|^2 \sin\theta\, d\theta\, d\varphi$$

$$\simeq \frac{2}{5}\frac{Z^4}{a_0^3 n^3} R_N^2 e^2 \delta_{l0}$$

where we have used the relation (see Appendix J)

$$[R_{nl}(0)]^2 = \left(\frac{Z}{a_0}\right)^3 \frac{4}{n^3}\delta_{l0}$$

A positive value of $W_n^{(1)}$ was expected because the potential energy increases due to the finite size of the nucleus (see Fig. 11.3). Thus

$$W_n \simeq W_n^{(0)} + W_n^{(1)} = -\frac{Z^2 m e^4}{2n^2\hbar^2}\left[1 - \frac{4}{5}\frac{Z^2 R_0^2 A^{2/3}}{a_0^2 n}\delta_{l0}\right] \tag{101}$$

where we have used the relation $R_N = R_0 A^{1/3}$, A being the mass number of the nucleus. For hydrogen

$$W_1^{(0)} \simeq -13.6 \text{ eV} \quad \text{and} \quad W_1^{(1)} \simeq 4 \times 10^{-9} \text{ eV} \tag{102}$$

which is indeed a small correction.

SOLUTION 11.10

For orbits inside the nucleus, we may write [see Eq. (100)]

$$H_0 = -\frac{\hbar^2}{2m_\mu}\nabla^2 - \frac{Ze^2}{R_N}\left(\frac{3}{2} - \frac{1}{2}\frac{r^2}{R_N^2}\right)$$

and

$$\begin{aligned} H' &= 0 && \text{for} \quad 0 \leqslant r \leqslant R_N \\ &= \frac{Ze^2}{R_N}\left(\frac{3}{2} - \frac{1}{2}\frac{r^2}{R_N^2}\right) - \frac{Ze^2}{r} && \text{for} \quad r > R_N \end{aligned}$$

where m_μ represents the mass of the muon. Now, H_0 is the same as one obtains in the 3-dimensional harmonic oscillator problem (see Problem 5.6). The radial part of the Schrödinger equation is of the form

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m_\mu}{\hbar^2}\left[E + \frac{3}{2}\frac{Ze^2}{R_N} - \frac{1}{2}\frac{Ze^2}{R_N^3}r^2 - \frac{l(l+1)\hbar^2}{2m_\mu r^2}\right]R(r) = 0$$

The energy levels are given by

$$E = -\frac{3}{2}\frac{Ze^2}{R_N} + \left(2p + l + \frac{3}{2}\right)\hbar\omega; \quad l = 0, 1, 2\ldots \quad p = 0, 1, 2\ldots \tag{103}$$

where

$$\omega = \left[\frac{Ze^2}{m_\mu R_N^3}\right]^{1/2} \tag{104}$$

Further

$$W^{(1)} = Ze^2\int_{R_N}^{\infty}|R_{pl}|^2\left[\frac{1}{R_N}\left(\frac{3}{2} - \frac{r^2}{2R_N^2}\right) - \frac{1}{r}\right]r^2\,dr \tag{105}$$

where the wave functions R_{pl} can be expressed in terms of confluent hypergeometric functions (see Problem 5.6).

As an example*, if we consider the $2P \rightarrow 1S$ transition in lead ($Z = 82$) and assume the nucleus to be a point charge, the energy liberated would be

$$\frac{m_\mu Z^2e^4}{2\hbar^2}\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{207Z^2}{2}\left(\frac{me^4}{\hbar^2}\right)\frac{3}{4} \simeq 14\text{MeV}$$

If we take into account the effect due to spin and due to relativistic effects the above value increases by 2 MeV to give 16 MeV; however, the experiments show that a photon of energy ~6 MeV is emitted. If we calculate the $1S$ energy level from Eq. (103) and $2P$ energy level from the expression

$$\frac{m_\mu Z^2e^4}{2n^2\hbar}$$

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*Data taken from Sokolov, Loskutov and Ternov (1966). A nice discussion on muonic atoms has been given by these authors.

then the energy difference between the $2P$ and $1S$ states comes out to be 3.6 MeV. If we now use Eq. (105) to incorporate the correction for the $1S$ energy state one obtains a value of 5 MeV which is close to the experimental value.

SOLUTION 11.11

If ψ_{nlm} represents the hydrogen atom wave functions then

$$\iiint \psi^*_{nl'm'} H' \psi_{nlm}\, d\tau = -\frac{1}{2mc^2}\iiint \psi^*_{nl'm'}\Big[E_n - V(r)\Big]^2 \psi_{nlm}\, d\tau$$

$$= -\frac{1}{2mc^2}\left\{\int_0^\infty \left[E_n + \frac{Ze^2}{r}\right] | R_{nl}(r) |^2 r^2\, dr\right\}\delta_{ll'}\,\delta_{mm'}$$

where E_n represents the energy levels of the hydrogen atom corresponding to the non-relativistic equation. The above equation tells us that we already have a representation in which H' is diagonal. Thus the relativity correction would be given by

$$W^{(1)}_{rel} = -\frac{1}{2mc^2}\left[E_n^2 + 2E_nZe^2\left\langle\frac{1}{r}\right\rangle + Z^2e^4\left\langle\frac{1}{r^2}\right\rangle\right]$$

$$= -\frac{1}{2mc^2}\left[\left(\frac{mZ^2e^4}{2n^2\hbar^2}\right)^2 - 2\left(\frac{mZ^2e^4}{2n^2\hbar^2}\right)Ze^2Z\left(\frac{me^2}{\hbar^2}\right)\frac{1}{n^2}\right.$$

$$\left. + Z^2e^4Z^2\left(\frac{me^2}{\hbar^2}\right)^2\frac{1}{n^3(l+\frac{1}{2})}\right]$$

$$= E_n\left(\frac{\alpha Z}{n}\right)^2\left[\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right] \tag{106}$$

where we have substituted the expressions for $\langle 1/r\rangle$ and $\langle 1/r^2\rangle$ from Appendix J and $\alpha = e^2/\hbar c \approx 1/137$ is the fine structure constant.

Thus the degeneracy is partially lifted. However, the results are not in agreement with the experimental data; one has to take into account the spin orbit interaction (see next problem).

SOLUTION 11.12

In a hydrogen-type atom, the unperturbed Hamiltonian (neglecting the spin orbit interaction) is given by

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}$$

The spin orbit interaction energy, H' is given by

$$H' = \frac{Ze^2}{2m^2c^2}\frac{1}{r^3}\mathbf{L}\cdot\mathbf{s} \tag{107}$$

where symbols have their usual meaning. Since

$$J^2 = L^2 + s^2 + 2\,\mathbf{L}\cdot\mathbf{s}$$

The Pauli operator for H' (see Sec. 9.5) is given by

$$(H')_P = \frac{Ze^2}{2m^2c^2}\,\frac{1}{r^3}\Big[(J^2)_P - (L^2)_P - (s^2)_P\Big]$$

Thus, the Pauli wave equation is given by

$$(H)_P\psi_P = \Big[(H_0)_P + (H')_P\Big]\psi_P = W\psi_P$$

where

$$(H_0)_P = \begin{pmatrix} H_0 & 0 \\ 0 & H_0 \end{pmatrix} = \begin{pmatrix} -\dfrac{\hbar^2}{2m}\nabla^2 - \dfrac{Ze^2}{r} & 0 \\ 0 & -\dfrac{\hbar^2}{2m}\nabla^2 - \dfrac{Ze^2}{r} \end{pmatrix}$$

and

$$\psi_P = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}$$

represents the Pauli wave function. The Pauli wave equation for the unperturbed Hamiltonian is given by (see Sec. 9.5 and Problem 9.12)

$$\begin{pmatrix} H_0 & 0 \\ 0 & H_0 \end{pmatrix}\begin{pmatrix} \psi_+^{(0)} \\ \psi_-^{(0)} \end{pmatrix} = W^{(0)}\begin{pmatrix} \psi_+^{(0)} \\ \psi_-^{(0)} \end{pmatrix} \tag{108}$$

or

$$W_0\,\psi_\pm^{(0)} = W^{(0)}\,\psi_\pm^{(0)}$$

Consequently, $W^{(0)}$ will simply represent the energy levels of hydrogen-type atom

$$W^{(0)} = E_n = -\frac{Z^2me^4}{2n^2\hbar^2} \tag{109}$$

and $\psi_\pm^{(0)}$ will be the hydrogen atom wave functions which are simply

$$R_{nl}(r)\,Y_{lm_l}(\theta, \varphi)$$

we have put a subscript l to m to distinguish it from m_s and m_j which correspond to the spin and total angular momentum operator respectively. Thus the Pauliwave functions for the spin up and the spin down states would be given by

$$(\psi_+^{(0)})_P = \psi(n, l, m_l, m_s = +\tfrac{1}{2}) = R_{nl}Y_{lml}\,|\uparrow\rangle = R_{nl}Y_{lml}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$= \begin{pmatrix} R_{nl}Y_{lml} \\ 0 \end{pmatrix} \tag{110}$$

and

$$(\psi_-^{(0)})_P = \psi(n, l, m_l, m_s = -\tfrac{1}{2}) = R_{nl} Y_{lm_l} \,|\downarrow\rangle$$

$$= \begin{pmatrix} 0 \\ R_{nl} Y_{lm_l} \end{pmatrix} \qquad (111)$$

In the absence of the spin orbit interaction, both the wavefunctions correspond to the same energy. Thus, in order to determine the splitting due to spin orbit interaction we must choose a representation in which H' is diagonal; i.e., we must choose such linear combinations of $(\psi_+^{(0)})_P$ and $(\psi_-^{(0)})_P$ in which $\mathbf{L} \cdot \mathbf{s}$ or J^2, L^2 and s^2 are well defined. This can easily be obtained by using Clebsch-Gordan coefficients (see Table 10.1 and Solution 9.12)

$$(\phi_1)_P = \phi(n, l, j = l + \tfrac{1}{2}, m_j)$$

$$= \sqrt{\frac{l + m_j + \frac{1}{2}}{2l + 1}}\; \psi(n, l, m_l = m_j - \tfrac{1}{2}, m_s = \tfrac{1}{2})$$

$$+ \sqrt{\frac{l - m_j + \frac{1}{2}}{2l + 1}}\; \psi(n, l, m_l = m_j + \tfrac{1}{2}, m_s = -\tfrac{1}{2})$$

$$= \begin{pmatrix} \sqrt{\dfrac{l + m_j + \frac{1}{2}}{2l + 1}}\; R_{nl}\, Y_{lm_j - \frac{1}{2}} \\ \sqrt{\dfrac{l - m_j + \frac{1}{2}}{2l + 1}}\; R_{nl}\, Y_{lm_j + \frac{1}{2}} \end{pmatrix} \qquad (112)$$

A similar expression can be written down for

$(\phi_2)_P = \phi(n, l, j = l - \tfrac{1}{2}, m_j)$. Now

$$\left.\begin{aligned} (J^2)_P\, \phi &= j(j + 1)\hbar^2 \phi \\ (L^2)_P\, \phi &= l(l + 1)\hbar^2 \phi \\ \text{and} \qquad (s^2)_P\, \phi &= \tfrac{3}{4}\hbar^2 \phi \end{aligned}\right\} \qquad (113)$$

Thus, the first order perturbation due to the spin orbit interaction would be given by

$$W_{s-0}^{(1)} = \int d\tau\, \phi^+ (H')_P\, \phi$$

$$= \frac{Ze^2}{4m^2c^2} \int d\tau\, \frac{1}{r^3}\, \phi^+ [(J^2)_P - (L^2)_P - (s^2)_P]\, \phi$$

$$= \frac{Ze^2}{4m^2c^2}\left[j(j + 1) - l(l + 1) - \frac{3}{4} \right]\hbar^2 \int d\tau\, \frac{1}{r^3}$$

$$\times \Bigg[\frac{l \pm m_j + \frac{1}{2}}{2l + 1}\, |R_{nl}|^2\, |Y_{l\, m_j - \frac{1}{2}}|^2 + \frac{l \mp m_j + \frac{1}{2}}{2l + 1}\, |R_{nl}|^2 \times |Y_{lm_j + \frac{1}{2}}|^2 \qquad (114)$$

where the upper and lower signs correspond to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ respectively. If we carry out the integration over the angles we obtain

$$W^{(1)}_{s-0} = \begin{cases} \dfrac{Ze^2}{4m^2c^2}\, l\hbar^2 \left\langle \dfrac{1}{r^3} \right\rangle & \text{for } j = l + \frac{1}{2} \\[2ex] -\dfrac{Ze^2}{4m^2c^2}(l+1)\hbar^2 \left\langle \dfrac{1}{r^3} \right\rangle & \text{for } j = l - \frac{1}{2} \end{cases} \tag{115}$$

where

$$\left\langle \frac{1}{r^3} \right\rangle = \int_0^\infty \frac{1}{r^3} |R_{nl}|^2 r^2\, dr = \frac{1}{n^3 l(l+\frac{1}{2})(l+1)} \left(\frac{Z}{\hbar^2/me^2} \right)^3 \tag{115}$$

(see appendix J). If we substitute this in Eq. (114), we obtain $W^{(1)}_{s-0}$; if we now add to this $W^{(0)}$ [see Eq. (109)], we would get the splitting of the level corresponding to the quantum number n. The final result is

$$W = W^{(0)} + W^{(1)}_{s-0} = \begin{cases} E_n\left[1 - \dfrac{Z^2\alpha^2}{n(l+1)(2l+1)}\right] & \text{for } j = l + \frac{1}{2} \\[2ex] E_n\left[1 + \dfrac{Z^2\alpha^2}{nl(2l+1)}\right] & \text{for } j = l - \frac{1}{2} \end{cases} \tag{116}$$

where $\alpha = e^2/\hbar c \simeq 1/137$ is the fine structure constant. Since E_n is a negative number, the level corresponding to $j = l + \frac{1}{2}$ will be higher. Thus, for the hydrogen atom ($Z = 1$), one obtains* for $n = 2$

$$\begin{aligned} W\left(n = 2, l = 1, j = \frac{3}{2}\right) - E(n = 2) &= -\frac{E_n}{12}\left(\frac{1}{137}\right)^2 \\ &\approx \frac{1.097 \times 10^5}{4 \times 12}\left(\frac{1}{137}\right)^2 \text{cm}^{-1} \\ &\approx 0.1217 \text{ cm}^{-1} \end{aligned}$$

Similarly

$$W(n = 2, l = 1, j = \tfrac{1}{2}) - E(n = 2) \approx -0.2435 \text{ cm}^{-1}$$
$$W(n = 2, l = 0, j = \tfrac{1}{2}) - E(n = 2) \approx +0.7304 \text{ cm}^{-1}$$
$$W(n = 1, l = 0, j = \tfrac{1}{2}) - E(n = 1) \approx +5.8435 \text{ cm}^{-1}$$

The corresponding spliting is not in agreement with the experimental data. We must also take into account the relativity correction (see Problem 11.11) which is given by Eq. (106). Substituting the values we get

$$W^{(1)}_{rel}(n = 2, l = 1) \approx -0.2130 \text{ cm}^{-1}$$

---

*In spectroscopy, the energy levels are measured in cm^{-1}; for this one has to divide W by hc. For example, the ground state energy for the hydrogen atom is

$$-\frac{1}{hc}\left(\frac{me^4}{2\hbar^2}\right) = -1.097 \times 10^5 \text{ cm}^{-1}.$$

and

$$W_{rel}^{(1)}\,(n = 2,\, l = 0) \approx -\,1.1870\ \text{cm}^{-1}$$

The splitting of the $n = 2$ level is shown in Fig. 11.4. [The data on the fine structure have been given and analysed by Ritchmeyer, Kennard and Lauritsen (1955), Secs. 120-121; see also Sokolov, Loskutov and Ternov (1966) Chapters 20 and 22]. Equations (104) and (114) may be combined in the form

$$W = W^{(0)} + W_{s-0}^{(1)} + W_{rel}^{(1)} = E_n\left[1 + \left(\frac{\alpha Z}{n}\right)^2\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right] \quad (117)$$

It should be mentioned that the perturbation treatment of the spin orbit interaction is not valid for $l = 0$ because $\langle 1/r^3\rangle$ diverges; however, Eq. (117) agrees with the results obtained by using Dirac theory (see Chapter 23) where this difficulty does not occur.

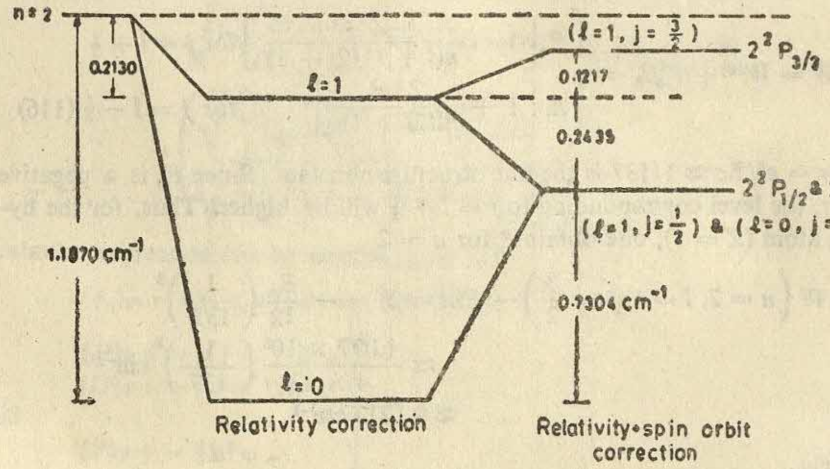

Fig. 11.4 The perturbations due to relativistic effects and spin orbit interaction for the $n = 2$ state of the hydrogen atom.

SOLUTION 11.15

The perturbation H' is given by

$$H' = \frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} \quad (118)$$

The terms e^2/R, e^2/r_{12}, $-e^2/r_{1B}$ and $-e^2/r_{2A}$ represent the interaction between the two protons, the two electrons, the first electron with the nucleus at B and the second electron with the nucleus at A respectively. We expand H' in powers of $1/R$

$$H' = \frac{e^2}{R}\Bigg[1 + R\left\{\frac{1}{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 + R - z_1)^2}\right\}^{1/2}$$

$$- R\left\{\frac{1}{x_1^2 + y_1^2 + (R - z_1)^2}\right\}^{1/2} - R\left\{\frac{1}{x_2^2 + y_2^2 + (z_2 + R)^2}\right\}^{1/2}\Bigg]$$

$$= \frac{e^2}{R}\Bigg[1 + \left\{1 + \frac{2(z_2 - z_1)}{R} + \frac{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}{R^2}\right\}^{-1/2}$$

$$- \left\{1 - \frac{2z_1}{R} + \frac{x_1^2 + y_1^2 + z_1^2}{R^2}\right\}^{-1/2} - \left\{1 + \frac{2z_2}{R} + \frac{x_2^2 + y_2^2 + z_2^2}{R^2}\right\}^{-1/2}\Bigg]$$

$$\approx \frac{e^2}{R^3}(x_1 x_2 + y_1 y_2 - 2z_1 z_2) \tag{119}$$

Let $\psi_k^{(0)}$ represent the wavefunctions of the unperturbed Hamiltonian and let $|k\rangle$ represent the corresponding eigenket; the ground state is assumed to correspond to $k = 1$. Thus

$$\psi_1^{(0)} = u_{100}(\mathbf{r}_1)\, u_{100}(\mathbf{r}_2) \tag{120}$$

where $u_{n\ell m}$ represent the hydrogen atom wavefunctions. Obviously

$$W_1^{(1)} = \langle 1 | H' | 1 \rangle = \iint d\tau_1\, d\tau_2\, [\psi_1^{(0)}]^* H' \psi_1^{(0)} = 0 \tag{121}$$

because integrals like

$$\int d\tau_1 x_1 [u_{100}(\mathbf{r}_1)]^2$$

would vanish. Now

$$W_1^{(2)} = \sum_k{}' \frac{|\langle 1 | H' | k \rangle|^2}{E_1 - E_k} > \frac{1}{E_1 - E_p} \sum_k{}' |\langle 1 | H' | k \rangle|^2$$

where the prime on Σ indicates that the term $k = 1$ has been omitted from the summation*. Further the pth state $(p \neq 1)$ corresponds to the lowest state for which $\langle 1 | H' | p \rangle$ does not vanish and the inequality follows from that fact that $E_k \geqslant E_p$. Now

$$\sum_k{}' |\langle 1 | H' | k \rangle|^2 = \sum_k |\langle 1 | H' | k \rangle|^2 - |\langle 1 | H' | 1 \rangle|^2$$

$$= \sum_k \langle 1 | H' | k \rangle \langle k | H' | 1 \rangle$$

$$= \langle 1 | H'^2 | 1 \rangle \tag{122}$$

*The Σ actually represents summation over discrete states and integration over continuum.

where we have used Eq. (121) and the completeness relation

$$\sum_k |k\rangle \langle k| = 1$$

[see Eq. (37) of Chapter 8]. Now

$$\begin{aligned}\langle 1 |H'^2| 1\rangle &= \frac{e^4}{R^6} \langle 1 | x_1^2x_2^2 + y_1^2y_2^2 + 4z_1^2z_2^2 + 2x_1x_2y_1y_2 \\ &\qquad - 4x_1x_2z_1z_2 - 4y_1y_2z_1z_2 | 1\rangle \\ &= \frac{e^4}{R^6}\, 6 \langle x_1^2\rangle^2 = \frac{6e^2a_0^4}{R^6}\end{aligned} \tag{123}$$

Further

$$E_1 = -\frac{me^4}{2\hbar^2} - \frac{me^4}{2\hbar^2} = -\frac{e^2}{a_0},$$

and the lowest state for which $\langle 1 | H' | k\rangle \neq 0$ corresponds to $n_1 = n_2 = 2$. Thus

$$E_p = -\frac{me^4}{8\hbar^2} - \frac{me^4}{8\hbar^2} = -\frac{e^2}{4a_0}$$

and

$$E_1 - E_p = -\frac{3}{4}\frac{e^2}{a_0}$$

Hence

$$W_1^{(2)} > -\frac{1}{\dfrac{3}{4}\dfrac{e^2}{a_0}} \frac{6e^4a_0^4}{R^6} = -\frac{8e^2a_0^5}{R^6}$$

or

$$W_1 \simeq W_1^{(0)} + W_1^{(2)} > -\frac{e^2}{a_0}\left[1 + \frac{8a_0^6}{R^6}\right] \tag{124}$$

CHAPTER TWELVE

The Variational Method

12.1 Introduction

In many cases stationary perturbation theory cannot be applied successfully as there may not be a closely related problem which is capable of exact solution.*

In this chapter, we shall describe the variational method for evaluating the energies of the ground state and the first few discrete states of a bound system, approximately. We shall then apply it to calculate the ground state energy of the helium atom and the hydrogen molecular ion.

12.2 The Basic Principle

Let ψ_n denote the exact set of eigenfunctions of the Hamiltonian H.

$$H\psi_n = E_n\psi_n \tag{1}$$

These eigenfunctions constitute a complete set of functions in the sense that an arbitrary bounded quadratically integrable function ϕ can be expanded in terms of the eigenfunctions. Thus we may write

$$\phi = \sum_n a_n\psi_n \tag{2}$$

Evidently, the quantity

$$\langle H\rangle = \int \psi_n^* \mathrm{H}\, \psi_n\, d\tau \tag{3}$$

yields the energy E_n, assuming that the ψ_n are normalized. Consider, now, the quantity

$$E_\phi = \frac{\int\phi^* H\phi d\tau}{\int\phi^*\phi d\tau} = \frac{\langle\phi\,|\,H\,|\,\phi\rangle}{\langle\phi\,|\,\phi\rangle} \tag{4}$$

(If we use normalized functions ϕ, E_ϕ resembles $\langle H\rangle$).

We can show that E_ϕ will always be larger than E_0, the lowest of the spectrum E_n. (E_0 is the ground state energy).

Before proving this simple result, one can see how this comes about. The effect of H on the ket vector $|\,\phi\rangle$ is, in general, to rotate it, except when $\phi\rangle$ is one of the eigenkets of H. Thus the scalar product, formed with the bra $\langle\phi\,|$ and $H\,|\,\phi\rangle$ will be an extremum for the precise case when $H\,|\,\phi\rangle$ and $|\,\phi\rangle$ point in the same direction.

---

*Even when the exact solution of the unperturbed Hamiltonian is known, the second order perturbation may be extremely difficult to calculate, as for example, the energy of a two-electron atom.

We have, on substitution for ϕ from Eq. (2) in Eq. (3)

$$E_\phi = \frac{\int(\Sigma\, a_n^* \psi_n^*\, H\, \Sigma\, a_n\psi_n)d\tau}{\int(\underset{n}{\Sigma}\, a_n^* \psi_n^*)\,(\underset{n}{\Sigma}\, a_n\psi_n d\tau)} \tag{5}$$

Since

$$\int \psi_n^* \psi_m \, d\tau = \delta_{nm} \tag{6}$$

we obtain

$$E_\phi = \frac{\underset{n}{\Sigma}\, a_n^* a_n E_n}{\underset{n}{\Sigma}\, a_n^* a_n} \tag{7}$$

Subtracting E_0, the energy of the ground state, from both sides of the equation, we have

$$E_\phi - E_0 = \frac{\underset{n}{\Sigma}\, |\, a_n\,|^2\,(E_n - E_0)}{\underset{n}{\Sigma}\, |\, a_n\,|^2} \tag{8}$$

Now

$$E_n \geqslant E_0$$

because by definition E_0 is the ground state energy, and since $|\, a_n\,|^2 \geqslant 0$ for all n, we must have

$$E_\phi - E_0 \geqslant 0$$

or
$$E_\phi \geqslant E_0 \tag{9}$$

This important inequality can be used to obtain an upper bound to the ground state energy E_0. We choose a suitable function ϕ known as the trial function which depends on a number of variable parameters $c_i (i = 1, \ldots, p)$. This trial function is substituted in Eq. (3) and the parameters are chosen so as to make E_ϕ a minimum by solving the p equations

$$\frac{\partial E_\phi}{\partial c_i} = 0 \quad (i = 1, 2, \ldots, p) \tag{10}$$

The minimum value of E determined in this way provides an upper bound to E_0, which will be close to the actual value if the trial function has a form closely resembling that of the actual ground state function ψ_0. Many different types of trial functions have been tried for the simple atoms and molecules, and some of these have been applied to much more complicated systems.

12.3 The Hydrogen Atom as an Example

In order to illustrate the use of the variational method, we apply it to the hydrogen atom problem. If we choose

$$\phi = A_1 \exp\left(-\alpha\,\frac{r}{a_0}\right)$$

we already have the correct form of the wavefunction [see Eq. (60) of Chapter 5]. We will calculate

$$E(\alpha) = \frac{\int \phi^* H \phi d\tau}{\int \phi^* \phi d\tau}$$

and set $\partial E/\partial\alpha = 0$, this will give us the value of α for which E is a minimum. We first normalize ϕ

$$1 = \int_0^\infty 4\pi r^2\, dr\, \phi^*\phi = 4\pi\, |A_1|^2 \int_0^\infty \exp\left[-\frac{2\alpha r}{a_0}\right] r^2\, dr$$

giving

$$A_1 = \left(\frac{\alpha^3}{\pi a_0^3}\right)^{1/2}$$

Thus

$$\phi = \left(\frac{\alpha^3}{\pi a_0^3}\right)^{1/2} \exp\left(-\alpha\frac{r}{a_0}\right)$$

Since $\phi(r)$ is now normalized, $E(\alpha) = \int \phi^* H \phi d\tau$. Further, since ϕ depends only on r, we need only keep the part of H which depends on r, i.e.,

$$H_{\text{radial}} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{e^2}{r} \tag{11}$$

The integrals are easy to evaluate and we obtain

$$E(\alpha) = \left[\frac{\hbar^2\alpha^2}{2ma_0^2} - \frac{e^2\alpha}{a_0}\right]$$

Setting $dE/d\alpha = 0$ gives $\alpha = me^2/\hbar^2 a_0 = 1$. Thus

$$E(\alpha)\,|_{\min} = -\frac{e^2}{2a_0} \tag{12}$$

which is the exact result, as it indeed should be, because we had started out with the correct form of ϕ.

It is instructive to see what we would obtain if we use other forms of the trial function (see also Problem 12.1). We choose

$$\phi = A \exp\left[-\alpha\left(\frac{r}{a_0}\right)^2\right]$$

Normalizing, we get

$$A = \left(\frac{2\alpha}{\pi a_0^2}\right)^{3/4}$$

The integrals are again easy to evaluate and one obtains

$$E(\alpha) = \left[\frac{3}{2}\alpha - 2^{3/2}\left(\frac{\alpha}{\pi}\right)^{1/2}\right]\frac{e^2}{a_0}$$

The minimum value of E is obtained when $\alpha = 8/9\pi$, the corresponding energy being

$$E(\alpha)|_{\min} = -0.85\,\frac{e^2}{2a_0} \tag{13}$$

In Fig. 12.1 we have plotted the following normalized functions

$$\psi_1 = \left(\frac{\alpha^3}{\pi a_0^3}\right)^{1/2} \exp\left(-\alpha\frac{r}{a_0}\right) \qquad \alpha = 1 \tag{14}$$

$$\psi_2 = \left(\frac{2\alpha}{\pi a_0^2}\right)^{3/4} \exp\left(-\alpha\frac{r^2}{a_0^2}\right) \qquad \alpha = \frac{8}{9\pi} \tag{15}$$

$$\psi_3 = \left(\frac{\alpha^5}{3\pi a_0^3}\right)^{1/2} \frac{r}{a_0} \exp\left(-\alpha\frac{r}{a_0}\right), \alpha = \frac{3}{2} \tag{16}$$

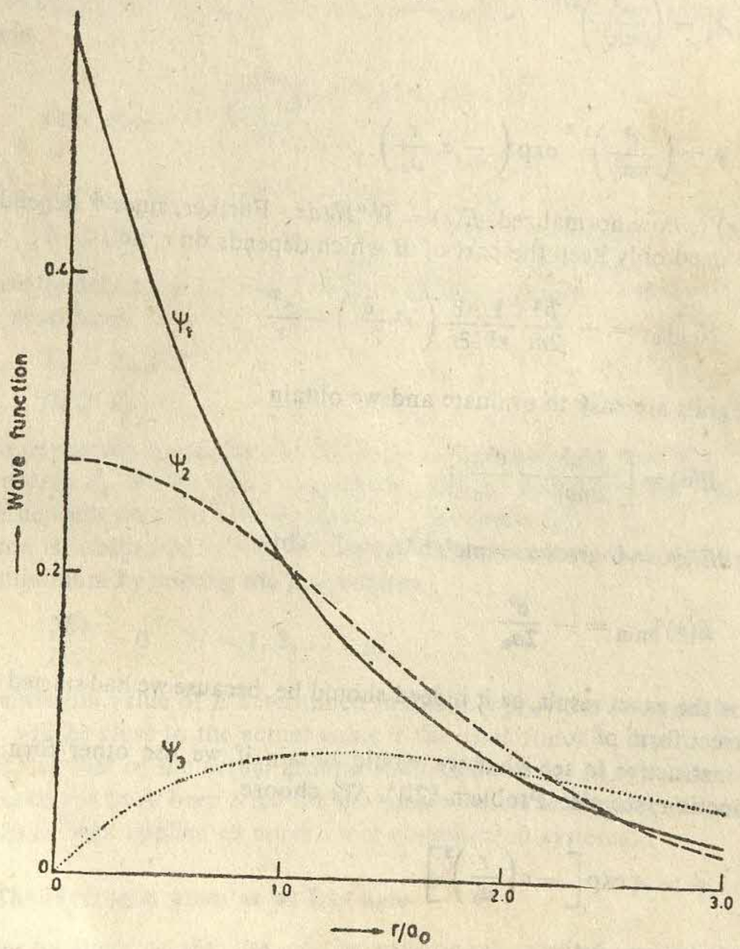

Fig. 12.1 The variation of the normalized trial functions (as given by Eqs. 14, 15 and 16).

the values of α are such that one obtains minimum energies for that particular form of function.

It can be seen that although ψ_3 is closer to the actual wavefunction ψ_1 than ψ_2 for large r, the energy obtained for ψ_2 is a better estimate. The reason is that for calculating energy eigenvalues, the wavefunction for large r does not contribute as much as for smaller values of r.

This observation illustrates an important point, namely, that the 'best' form of wavefunction depends on the particular problem at hand. If we are interested primarily in the large r behaviour of the wavefunction for calculating a physical quantity for the system, the function that yields a better energy estimate may not nevertheless be an appropriate wavefunction.

12.4 The Helium Atom

Another illustration of the variational method is the application to the ground state of helium. If we assume that the two 1s electrons move independently in the field of the nucleus (i.e., neglecting their mutual repulsion), the wavefunction will be

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \left(\frac{Z^3}{\pi a_0^3}\right) e^{-Zr_1/a_0}\, e^{-Zr_2/a_0}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the co-ordinates of the two electrons, with the origin at the nucleus and $Z = 2$, the nuclear charge (see Fig. 15.1).

The interaction of the electrons will result in their being held a little more loosely by the nucleus. We therefore choose a trial function of the form

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z'^3}{\pi a_0^3} \exp\left[-\frac{Z'r_1}{a_0}\right] \exp\left[-\frac{Z'r_2}{a_0}\right] \tag{17}$$

with Z' representing an effective nuclear charge and regard it as a variational parameter; we expect the best value of Z' to be somewhat less than the nuclear charge. Since ϕ is normalized,

$$E(Z') = \iint \phi^* H \phi \, d\tau_1 \, d\tau_2$$

The above integral has been evaluated in Sec. 15.4 and Problem 15.2. The minimum value is

$$E_0 = -2\left(Z - \frac{5}{16}\right)^2 \frac{e^2}{2a_0} = -2\left(Z - \frac{5}{16}\right)^2 \times 13.6 \text{ eV} \tag{18}$$

which occurs when

$$Z' = Z - \frac{5}{16} \tag{19}$$

This value of the energy is better than the value obtained from first order perturbation theory (see Sec. 15.3). Putting $Z = 2$, we get

$$E_0 = -\left(\frac{27}{16}\right)^2 \frac{e^2}{a_0} = -2.85\frac{e^2}{a_0} \tag{20}$$

The experimental value for the minimum energy required to remove both the electrons from a helium atom is 2.904 e^2/a_0. It is worthwhile pointing out that a large number of trial functions have been used to obtain the ground state energy of the helium atom. Some of the trial functions used and the correspondind ground state energies are tabulated in Table 12.1. It should be noted that in general, the accuracy of the calculated value of the ground state energy increases with increase in the number of terms.

TABLE 12.1 Variation Functions for the Normal Helium Atom*

(Symbols $s = \frac{r_1 + r_2}{a_0}$, $t = \frac{r_1 - r_2}{a_0}$, $u = r_{12}/a_0$

Experimental value** $W = -5.8736\, R_{\text{He}}hc$)

*Variation function, with best values of constants****	*Energy (in units of $-R_{\text{He}}hc$)*	*Deviation from experiment (in units of $-R_{\text{He}}hc$)*
1. e^{-2s}	5.50	0.31
2. $e^{-Z's}$, $Z' = \frac{27}{16} = 1.6875$	5.6953	0.1120
3. $e^{-Z's} \cosh ct$, $Z' = 1.67$, $c = 0.48$	5.7508	0.0565
4. $e^{-Z's}(1 + c_2t^2)$, $Z' = 1.69$, $c_2 = 0.142$	5.7536	0.0537
5. $e^{-Z's} e^{cu}$, $Z' = 1.86$, $c = 0.26$	5.7792	0.0281
6. $e^{-Z's}(1 + c_1u)$, $Z' = 1.849$, $c_1 = 0.364$	5.7824	0.0249
7. $e^{-Z's}(1 + c_1u + c_2t^2)$, $Z' = 1.816$, $c_1 = 0.30$, $c_2 = 0.13$	5.80488	0.00245
8. $e^{-Z's}(1 + c_1u + c_2t^2 + c_3s + c_4s^2 + c_5u^2)$ $Z' = 1.818$, $c_1 = 0.353$, $c_2 = 0.128$, $c_3 = -0.101$, $c_4 = 0.033$, $c_5 = -0.032$	5.80648	0.00085

*After Pauling and Wilson (1935), Sec. VIII—29*d*.

**$R_{\text{He}} = \frac{2\pi^2\mu e^4}{h^3c} = 109722.4\ \text{cm}^{-1}$. ($\mu$ is the reduced mass of the electron and the nucleus).

***The normalization factor is omitted of these functions, 1 is due to Unsold, 2 to Kellner, 3 to Eckart and Hylleraas and the remainder to Hylleraas.

12.5 Application to Excited States

Suppose we choose a ket $|\phi\rangle$ which has no component along the *ground state axis*, i.e., $|\phi\rangle$ lies entirely in the *plane* of the remaining eigenkets in the Hilbert space. If we now vary $|\phi\rangle$, (keeping the variation within this *plane*), we ought to arrive at the best estimate for the energy of the first excited state.

We do this by first restricting our choice ϕ to be orthogonal to ψ_0. Let

$$\phi = \chi - \psi_0 \int \psi_0^* \chi \, d\tau \tag{21}$$

Since ϕ is now orthogonal to ψ_0 (as can be easily seen by evaluating $\int \phi^* \psi_0 \, d\tau$), we have

$$\phi = \sum_{1}^{\infty} a_n \psi_n$$

the coefficient a_0 being zero. We can now evaluate E_ϕ as before and show that

$$E_\phi - E_1 = \frac{\sum_{1}^{\infty} |a_n|^2 (E_n - E_1)}{\sum_{1}^{\infty} |a_n|^2}$$

and conclude $E_\phi > E_1$ using the same arguments as before.

Thus, one chooses an appropriate form χ with a set of variable parameters, then define ϕ as in Eq. (21) and go through the variation procedure.

Evidently, this procedure can be continued for higher states; we define

$$\phi = \chi - \sum_{n=0}^{N-1} \psi_n \int \psi_n^* \chi \, d\tau \tag{22}$$

ϕ is now orthogonal to the lowest $N-1$ states and we can estimate the energy of the Nth state. However, the procedure is quite cumbersome as one goes to higher levels. It is sometimes possible to choose a trial function ϕ directly from symmetry considerations so that orthogonality to lower state eigenfunctions is ensured.

12.6 Linear Variation Functions

A trial function can also be chosen as a linear combination of a set of complete orthonormal functions u_n

$$\psi = \sum_{n=1}^{m} c_r u_n \tag{23}$$

The variational energy is therefore given by

$$E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} = \frac{\sum_{n}\sum_{m} c_n^* c_m H_{nm}}{\sum_{n} |c_n|^2}$$

or $$E \sum_n |c_n|^2 = \sum_n \sum_m c_n^* c_m H_{nm} \tag{24}$$

where $$H_{nm} = \int u_n^* H u_m d\tau \tag{25}$$

Differentiating Eq. (24) with respect to c_k and setting $\partial E/\partial c_k = 0$, we obtain*

$$\sum c_n^* H_{nk} - E c_k^* = 0 \tag{26}$$

For nontrival solutions the determinant must vanish. Thus

$$|H_{ij} - E\delta_{ij}| = 0;\ i, j = 1, 2, \ldots, m \tag{27}$$

Eq. (27) is known as the secular equation. Equation (27) will, in general, give m roots of E. For a particular value of E, the coefficient c_k can be found by using Eq. (26) and the normalization condition

$$\sum_n |c_n|^2 = 1 \tag{28}$$

The lowest root of E and the correspondingwave function represent approximations to the energy and the wavefunction of the ground state of the system. Other roots and the corresponding wavefunctions represent approximation to the excited states.

Often, it is more convenient to use a set of basis functions which are not necessarily orthogonal. In that case, the secular equation takes the form

$$|H_{ij} - S_{ij}E| = 0 \tag{29}$$

where $$S_{ij} = \int u_i^* u_j d\tau \tag{30}$$

is known as the overlap integral.

12.7 The H_2^+ Ion

As an example of the linear combination method, we consider the H_2^+ ion. The Hamiltonian, neglecting the nuclear kinetic energy and the spin orbit interaction, is given by

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \tag{31}$$

where $r_A = |\mathbf{r} - \mathbf{R}_A|$, $r_B = |\mathbf{r} - \mathbf{R}_B|$, $R = |\mathbf{R}_A - \mathbf{R}_B|$,

$\mathbf{r}$ being the position of the electron, $\mathbf{R}_A$ and $\mathbf{R}_B$ being the positions of the two protons.

If R is large, then there will be a large probability for the electron to be either near A or near B but not both. Indeed, in the former case we have

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*What would be the equation if we had differentiated Eq. (24) with respect to c_k^*?

approximately a 1*s* hydrogen atom wavefunction centred at *A* and in the latter case at *B*. This suggests that we use a linear combination as a trial function, i.e.,

$$\psi = c_A u_{1A} + c_B u_{1B} \tag{32}$$

Note that the wavefunctions u_{1A} and u_{1B} which are the 1*s* wavefunctions at *A* and *B*, are *not* orthogonal. A single electron wavefunction as above is called a molecular orbital. This particular form of a linear combination of atomic *orbitals* making a molecular orbital is called LCAO-MO for short. We now use Eq. (29). The normalized wavefunctions are given by

$$\begin{aligned} u_{1A} &= \left(\frac{1}{\pi a_0^3}\right)^{1/2} \exp\left[\frac{-r_A}{a_0}\right] \\ u_{1B} &= \left(\frac{1}{\pi a_0^3}\right)^{1/2} \exp\left[\frac{-r_B}{a_0}\right] \end{aligned} \tag{33}$$

The integrals in Eq. (29) should now be evaluated

$$S_{AA} = \frac{1}{\pi a_0^3}\int \exp\left[-(2r_A/a_0)\right] d\tau = 1 = S_{BB}$$

$$\begin{aligned} S_{AB} = S_{BA} &= \frac{1}{\pi a_0^3}\int \exp\left[(-r_A/a_0) - (r_B/a_0)\right] d\tau \\ &= S, \text{ say} \end{aligned}$$

$$\begin{aligned} H_{AA} = H_{BB} &= \frac{1}{\pi a_0^3}\int \exp\,(r_A/a_0)\left[-\frac{\hbar^2}{2m}\nabla^2 \right. \\ &\qquad \left. -\frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R}\right] \exp\,(-r_A/a_0)\, d\tau \\ &= \frac{e^2}{R} - \frac{e^2}{2a_0} - \frac{e^2}{\pi a_0^3}\int \frac{1}{r_B}\exp\,(-2r_A/a_0)\, d\tau \end{aligned}$$

and

$$\begin{aligned} H_{AB} = H_{BA} &= \frac{1}{\pi a_0^3}\int \exp\,(r_A/a_0)\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_A} \right. \\ &\qquad \left. -\frac{e^2}{r_B} + \frac{e^2}{R}\right] \exp\,(-r_B/a_0)\, d\tau \\ &= \left(\frac{e^2}{R} - \frac{e^2}{2a_0}\right) S_{AB} - \frac{e^2}{\pi a_0^3}\int \frac{1}{r_A}\exp\,(-r_A/a_0) \\ &\qquad \times \exp\,(-r_B/a_0)\, d\tau \end{aligned}$$

In order to evaluate the integrals in the expressions for S_{AB}, H_{AA} and H_{AB}, it is convenient to introduce the confocal elliptic co-ordinates

$$\mu = \frac{r_A + r_B}{R},\ \nu = \frac{r_A - r_B}{R} \tag{34}$$

and the azimuthal angle φ. Obviously

$$1 < \mu < \infty;\ -1 \leqslant \nu \leqslant +1;\ 0 \leqslant \varphi \leqslant 2\pi$$

and

$$\int F d\tau = \int_1^{\infty} d\mu \int_{-1}^{+1} d\nu \int_0^{2\pi} d\varphi \, \frac{R^3}{8} (\mu^2 - \nu^2) F(\mu, \nu, \varphi) \tag{35}$$

The integrations can easiliy be carried out. The results are as follows

$$S_{AB} = S_{BA} = [1 + \xi + \tfrac{1}{3}\xi^2]e^{-\xi} \tag{36a}$$

$$H_{AA} = H_{BB} = \left[-\frac{1}{2} + \left(\frac{1}{\xi} + 1\right)e^{-2\xi}\right]\frac{e^2}{a_0} \tag{36b}$$

$$H_{AB} = H_{BA} = \left[\left(\frac{1}{\xi} - \frac{1}{2}\right)S_{AB} - (1 + \xi)e^{-\xi}\right]\frac{e^2}{a_0} \tag{36c}$$

where $\xi = R/a_0$. Now the secular equation [Eq. (29)] is of the form

$$\begin{vmatrix} H_{AA} - S_{AA}\,E & H_{AB} - S_{AB}\,E \\ H_{BA} - S_{BA}\,E & H_{BB} - S_{BB}\,E \end{vmatrix} = 0 \tag{37}$$

Thus $(H_{AA} - E)^2 = (H_{AB} - S_{AB}E)^2$ (38)

or $E_{\pm} = \dfrac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}}$ (39)

The corresponding wavefunctions can easily be found

$$\psi_+ = \frac{1}{\sqrt{2}\,(1 + S_{AB})^{1/2}} (u_{1A} + u_{1B}) \tag{40}$$

$$\psi_- = \frac{1}{\sqrt{2}(1 - S_{AB})^{1/2}} (u_{1A} - u_{1B}) \tag{41}$$

Obviously ψ_+ is symmetric with respect to the interchange of the nuclei and ψ_- is antisymmetric.

Since the dissociation energy of the deuteron is $E_H + E_{H^+} - E_{H_2^+}$ we define

$$\mathcal{E}_{\pm} = E_{\pm} + \frac{e^2}{2a_0} = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}} + \frac{e^2}{2a_0} \tag{42}$$

We substitute the expressions for H_{AA}, H_{AB} and S_{AB} from Eq. (36) and calculate $\mathcal{E}_{\pm}$ as a function of ξ (see Fig. 12.2). The quantity $\mathcal{E}_+$ (which corresponds to the symmetric state) has a minimum value* for $\xi \approx 2.4$ giving $R \approx 1.3$ Å, the corresponding value of $\mathcal{E}_+$ being -1.76 eV. Experimentally $R \approx 1.06$ Å and the dissociation energy is 2.8 eV. A better agreement between theory and experiment is obtained by introducing a variational parameter in the trial function (see Problem 12.4).

We may point out certain shortcomings of the chosen trial function. For example, if we let $R \to 0$ we should obtain the He$^+$ ion the ground state energy of

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*The wavefunction ψ_+ which leads to negative energy values is known as a *bonding orbital*; on the other hand, since ψ_- leads to positive energy values, it is known as an *anti-bonding orbital*.

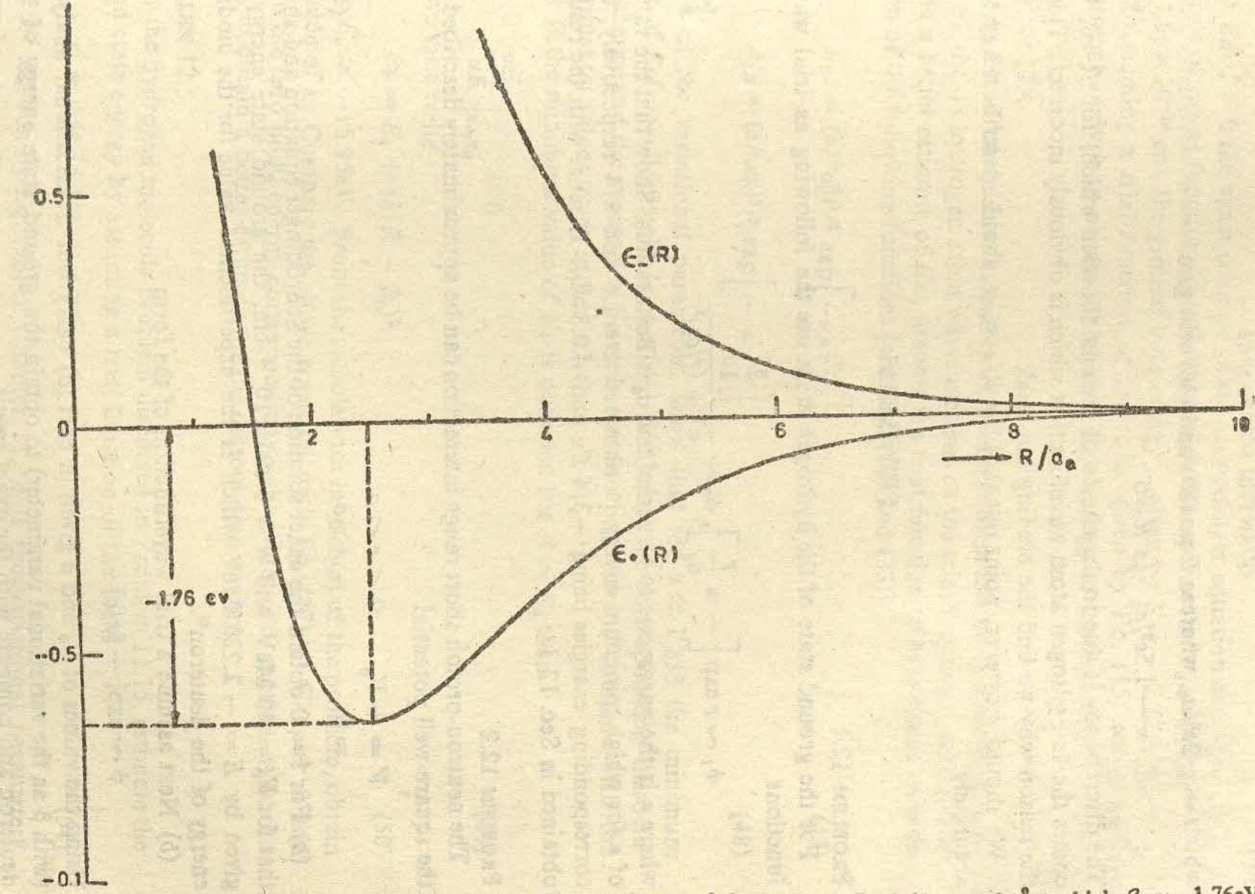

Fig. 12.2 The variation of $\mathcal{E}_\pm$ as a function of R/a_0. The minimum of $\mathcal{E}_+$ occurs at $R \approx 2.45\ a_0 \approx 1.3\text{Å}$ at which $\mathcal{E}_+ \approx -1.76\text{eV}$.

which is $-2e^2/a_0$, whereas Eqs. (39) and (36) will give

$$E_+ \to -1.5e^2/a_0 \quad \text{as } R \to 0 \tag{43}$$

The discrepancy is due to the choice of the trial function which, for $R\to 0$, becomes the 1*s* hydrogen atom wavefunction which is obviously incorrect. This is the reason why we find the binding too weak.

We should, however, point out that for $R\to\infty$, ψ_+ should describe the system accurately.

PROBLEMS

PROBLEM 12.1

For the ground state of the hydrogen atom use the following as trial wavefunctions

$$\phi_1 \sim r\exp\left[-\alpha\frac{r}{a_0}\right],\ \phi_2 \sim \frac{1}{\alpha^2+(r/a_0)^2} \tag{43}$$

where α is the parameter to be varied and a_0 is Bohr radius. Show that the values of α for which minimum energy is obtained are 1.5 and $\pi/4$ respectively, the corresponding energies being $-3/4\ E_H$ and $-0.81E_H$. Discuss with the results obtained in Sec. 12.3.

PROBLEM 12.2

The neutron-proton short range interaction can be approximately described by the square well potential

$$\begin{aligned} V &= -V_0 \qquad 0<r<a \\ &= 0 \qquad\quad r>a \end{aligned} \tag{44}$$

(*a*) For $l=0$ obtain the exact solution of the Schrödinger equation and show that for $V_0 = 40$ MeV and $a = 1.896\times 10^{-13}$ cm, the ground state energy is given by $E = -2.223$ MeV which is the experimental value for the binding energy of the deuteron*.

(*b*) Next assume a trial wavefunction of the form

$$\phi \sim \exp[-\beta r/a] \tag{45}$$

Using the values of V_0 and a given in part (*a*) carry out a variational analysis (with β as the variational parameter) to obtain the ground state energy of the deuteron and compare with the exact result.

PROBLEM 12.3

The neutron-proton interaction can also be described by the exponential potential

$$V = -V_0e^{-r/a} \tag{46}$$

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*In Problems 12.2 (*a*) and 12.3 (*a*) the value of V_0 and a are chosen such that the minimum energy eigenvalue agrees with the experimental value.

(a) Eor $l = 0$ the exact solution of the Schrödinger equation can be obtained in terms of Bessel functions (see Problem 5.7). Show that for $V_0 = 40$ MeV and $a = 1.85 \times 10^{-13}$ cm, the ground state energy is given by $E = -2.223$ MeV.

(b) Assuming a trial function of the form given by Eq. (45) carry out a variational analysis to obtain the ground state energy of the deuteron.

PROBLEM 12.4

(*a*) In Sec. 12.4 we have solved the H_2^+ ion problem assuming linear combination of the 1*s* hydrogen atom wavefunctions as the trial function. In order to obtain a better estimate of $E_\pm$, assume the trial function to be a linear combination of the following functions [see Eqs. (32) and (33)]

$$u_{1A} = (\alpha/\pi a_0^3)^{1/2} \exp\left[-\alpha \frac{r_A}{a_0}\right] \tag{47}$$

$$u_{1B} = (\alpha/\pi a_0^3)^{1/2} \exp\left[-\alpha \frac{r_B}{a_0}\right] \tag{48}$$

with α as the variational parameter. Show that for $\alpha \approx 1.238$ the minimum value of $E_+(= -15.95$ eV) is obtained. Calculate the corresponding dissociation energy and the separation between the two protons and compare with the experimental values given in Sec. 12.4.

(b) If the minimum value of E_+ is obtained for $R = R_0$ then

$$\left.\frac{dE_+}{dR}\right|_{R=R_0} = 0 \tag{49}$$

and we may write

$$E_+ = E_0 + \tfrac{1}{2}k(R - R_0)^2 \tag{50}$$

where $E_0 \approx -15.95$eV. From the calculations in part (*a*) of the problem, obtain the value of k. Compare the above equation with Eq. (77) of Chapter 5 and obtain the zero point energy corresponding to the vibrational motion. Add this to E_+ to obtain a better estimate for the dissociation energy.

PROBLEM 12.5

For the hydrogen molecule problem discussed in Problem 11.15, estimate the ground state energy by assuming a trial function of the form

$$\phi = u_0(\mathbf{r}_1, \mathbf{r}_2)\,(1 + AH') \tag{51}$$

where H' is given by Eq. (98) of Chapter 11, A is the variational parameter* (assumed to be real) and

$$u_0(\mathbf{r}_1, \mathbf{r}_2) = u_{100}(\mathbf{r}_1) u_{100}(\mathbf{r}_2) \tag{52}$$

$u_{100}(\mathbf{r}_1)$ and $u_{100}(\mathbf{r}_2)$ being the wavefunctions corresponding to the ground state of the hydrogen atom, the co-ordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ are defined in Fig. 11.2.

---

*This problem is adapted from Schiff (1968); the justification for such a choice of the trial function is also given there.

SOLUTIONS

SOLUTION 12.2

(a) The solution of the radial part of the Schrödinger equation for the square well potential is discussed in Secs. 19.5.2 and 19.5.3. We write $E = -B$ where B is the binding energy of the deuteron. The equation that determines the energy eigenvalues for $l = 0$ is [see Eq. (85) of Chapter 19]

$$\cot k_1 a = -\kappa/k_1 = -[B/(V_0 - B)]^{1/2} \tag{53}$$

where $\kappa^2 = 2\mu B/\hbar^2$ and $k_1^2 = 2\mu(V_0 - B)/\hbar^2$.

Now $\mu = m_n m_p/(m_n + m_p) \approx 1.67 \times 10^{-24}$ g. For $V_0 \simeq 40$ MeV, $a \simeq 1.896 \times 10^{-13}$ cm we obtain $B \simeq 2.223$ MeV.

(b) The normalized trial wavefunction is given by

$$\phi = \left[\frac{\beta^3}{\pi a^3}\right]^{1/2} \exp\left[-\frac{\beta r}{a}\right] \tag{54}$$

Thus

$$E_\beta = \frac{\beta^3}{\pi a^3}\int_0^\infty e^{-\beta r/a}\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - V(r)\right]e^{-\beta r/a}\, 4\pi r^2 dr \tag{55}$$

Substituting for $V(r)$ from Eq. (44) and carrying out the integration, we get

$$E_\beta = \frac{\hbar^2}{2\mu a^2}\left[\beta^2 - 2\gamma\{1 - (1 + 2\beta + 2\beta^2)e^{-2\beta}\}\right] \tag{56}$$

where

$$\gamma = \frac{\mu V_0 a^2}{\hbar^2} \simeq 1.73 \tag{57}$$

The minimum occurs when $dE_\beta/d\beta = 0$ giving

$$\beta e^{-2\beta} = \frac{1}{4\gamma} = 0.1445 \tag{58}$$

On solving the above equation we get $\beta \simeq 0.93$. Thus

$$E_\beta \simeq -1.43 \text{ MeV}$$

As can be seen the error is quite large which is due to the fact that the choice of the trial function is poor.

SOLUTION 12.3

(*a*) Referring to the solution of Problem 5.7, we have

$$g = \left[\frac{8\mu V_0 a^2}{\hbar^2}\right]^{1/2} \simeq 3.64 \tag{59}$$

The solution of the equation $J_\nu(g) = 0$ gives

$$\nu = \left[\frac{8\mu B a^2}{\hbar^2}\right]^{1/2} \simeq 0.858 \tag{60}$$

giving $B = 2.223$ MeV.

(*b*) We substitute for $V(r)$ from Eq. (46) in Eq. (55) and carry out the integration to obtain

$$E_\beta = \frac{\hbar^2}{2\mu a^2}\left[\beta^2 - \frac{8\gamma\beta^3}{(1+2\beta)^3}\right] \tag{61}$$

where

$$\gamma = \frac{\mu V_0 a^2}{\hbar^2} \simeq 1.655$$

The minimum occurs when $dE_\beta/d\beta = 0$ giving

$$\frac{(1+2\beta)^4}{\beta} = 24\gamma = 39.73 \tag{62}$$

On solving the above equation we get $\beta = 0.6088$. Thus

$$E_\beta = -2.14 \text{ MeV}$$

SOLUTION 12.4

The analysis is similar to the one given in Sec. 12.4; the result for E_+ is

$$E_+ = \left[-\frac{\alpha^2}{2} + \frac{\alpha(\alpha-1) - \frac{\alpha}{\zeta}\{1-(1+\zeta)e^{-2\zeta}\} + \alpha(\alpha-2)(1+\zeta)e^{-\zeta}}{1+(1+\zeta+\frac{1}{3}\zeta^2)e^{-\zeta}} + \frac{\alpha}{\zeta}\right]\frac{e^2}{a_0} \tag{63}$$

where $\zeta = \alpha\xi = \alpha R/a_0$. For $\alpha = 1$ we will get the results of Sec. 12.4. Now we may write the above equation in the form

$$E_+ = \alpha F_1(\zeta) + \alpha^2 F_2(\zeta) \tag{64}$$

where

$$F_1(\zeta) = \left[\frac{-1 - \frac{1}{\zeta}\{1-(1+\zeta)e^{-2\zeta}\} - 2(1+\zeta)e^{-\zeta}}{1+(1+\zeta+\frac{1}{3}\zeta^2)e^{-\zeta}} + \frac{1}{\zeta}\right]\frac{e^2}{a_0} \tag{65}$$

and

$$F_2(\zeta) = \left[-\frac{1}{2} + \frac{1+(1+\zeta)e^{-\zeta}}{1+(1+\zeta+\frac{1}{3}\zeta^2)e^{-\zeta}}\right]\frac{e^2}{a_0} \tag{66}$$

We take α and ζ as two independent parameters. Setting $dE_+/d\alpha = 0$, we get

$$\alpha = -F_1(\zeta)/2F_2(\zeta) \tag{67}$$

Thus

$$E_+ = -\frac{[F_1(\zeta)]^2}{4F_2(\zeta)} \tag{68}$$

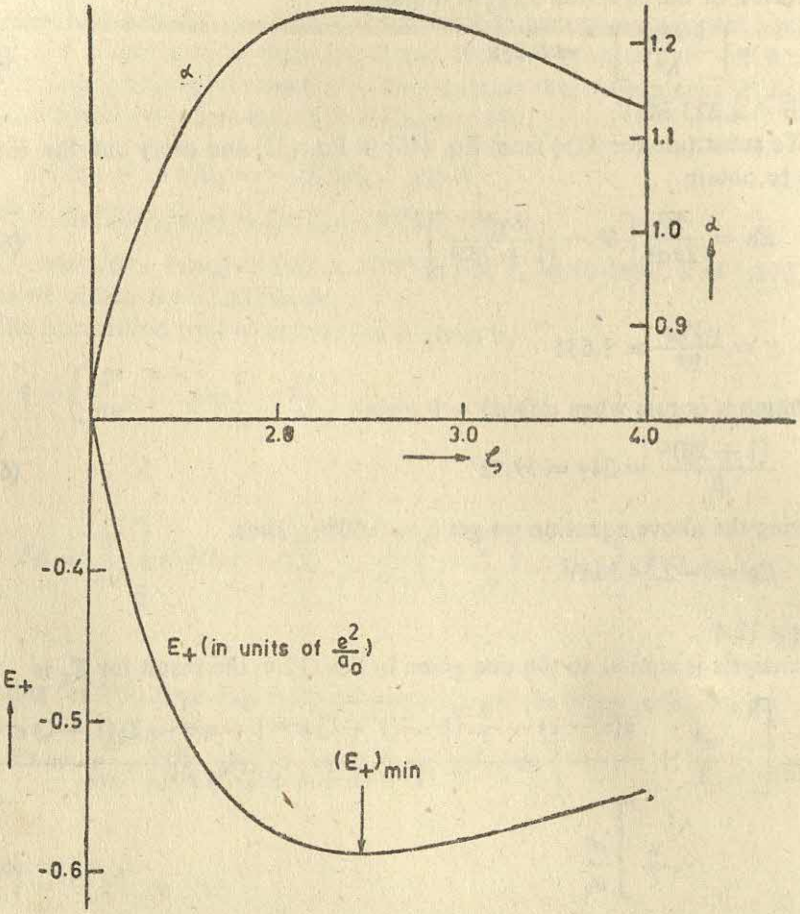


Fig. 12.3 The variation of E_+ and α with ζ. The minimum value of E_+ ($\simeq -0.5865\ e^2/a_0 \simeq -15.95$ eV) occurs at $\zeta = 2.48$ at which $\alpha \simeq 1.238$.

These two equations enable us to plot α and E_+ as a function of ζ (see Fig. 12.3) the minimum value of E_+ ($\simeq -0.5865\ e^2/a_0 \simeq -15.95$ eV) occurs at $\zeta \simeq 2.48$ for which $\alpha \simeq 1.238$.

Thus

$$\text{Dissociation energy} = E_H - E_{H_2^+} \simeq -13.6 + 15.95 \text{ eV} = 2.35 \text{ eV}$$

$$R = \frac{\zeta}{\alpha} a_0 \simeq 2.003\ a_0 \approx 1.06\ \text{Å}$$

(*b*) By differentiating E_+ one can show

$$\frac{d^2E_+}{d\zeta^2} \simeq 0.092\ \frac{e^2}{a_0}$$

Thus

$$\frac{d^2E_+}{dR^2} \simeq 0.092\,\frac{e^2}{a_0}\left(\frac{\alpha}{a_0}\right)^2 \simeq 1.369 \times 10^{17}\ \text{erg/cm}^2$$

Since $\mu \approx \frac{1}{2} m_n \approx 1.67 \times 10^{-24}$ g, we have, using Eq. (123) of Chapter 5, the following value for the zero point vibrational energy

$$E\text{vib} = \frac{\hbar}{2}\sqrt{\frac{k}{\mu}} = \frac{1}{2} \times 10^{-27}\sqrt{\frac{1.369 \times 10^{17}}{1.67 \times 10^{-24}}} \simeq 1.81 \times 10^{-13}\ \text{erg}$$

$$\approx 0.11\ \text{eV}$$

Thus the dissociation energy becomes 2.24 eV.

SOLUTION 12.5

$$E_\phi = \frac{\int \phi^* H \phi\, d\tau}{\int \phi^* \phi\, d\tau}$$

where $H = H_0 + H'$ (see Problem 11.15), $d\tau = d\mathbf{r}_1, d\mathbf{r}_2$ and the integral is over a six dimensional space. Now

$$u_0 = u_{100}(\mathbf{r}_1)\, u_{100}(\mathbf{r}_2) = \frac{1}{\pi a_0^3} \exp\left(-\frac{r_1 + r_2}{a_0}\right)$$

and $$H_0 u_0 = E_0 u_0,\ E_0 = -\frac{e^2}{2a_0} - \frac{e^2}{2a_0} = -\frac{e^2}{a_0}$$

Thus, $$\begin{aligned}\int \phi^* \phi\, d\tau &= \int u_0^2 d\tau + 2A \int u_0 H' u_0\, d\tau + A^2 \int u_0 H'^2 u_0\, d\tau \\ &= 1 + A^2 \int u_0 H'^2 u_0\, d\tau\end{aligned}$$

where we have used the relation

$$\int u_0 H' u_0 d\tau = 0$$

which can be verified by direct integration. Further,

$$\begin{aligned}\int \phi^* H \phi\, d\tau &= \int u_0(1 + AH')(H_0 + H')\, u_0(1 + AH')\, d\tau \\ &= \int u_0 H_0 u_0 d\tau + \int u_0 H' u_0 d\tau \\ &\qquad + A\left[\int u_0 H' H_0 u_0 d\tau + \int u_0 H_0 (u_0 H')\, d\tau\right. \\ &\qquad \left. + \int u_0 H' u_0 H' d\tau + \int u_0 H'^2 u_0 d\tau\right] \\ &\qquad + A^2\left[\int u_0 H' H_0 (u_0 H')\, d\tau + \int u_0 H'^3 u_0 d\tau\right] \\ &= E_0 + A\left[E_0 \int u_0 H' u_0 d\tau + E_0 \int u_0 u_0 H' d\tau\right. \\ &\qquad \left. + 2 \int u_0 H'^2 u_0\, d\tau\right] \\ &= E_0 + 2A \int u_0 H' u_0 d\tau\end{aligned}$$

the other integrals going to zero. Thus

$$\begin{aligned}E_\phi &= \frac{E_0 + 2A \int u_0 H'^2 u_0 d\tau}{1 + A^2 \int u_0 H'^2 u_0 d\tau} \\ &\approx E_0 + (2A - A^2 E_0) \int u_0 H'^2 u_0 d\tau\end{aligned}$$

Setting $dE/dA = 0$, we get $A = 1/E_0$. Thus the minimum value of E_ϕ is given by

$$E_\phi = E_0 + \frac{1}{E_0}\int u_0 H'^2 u_0 d\tau$$

The integral is evaluated in Problem 11.15, on substitution we get

$$E_\phi = E_0 - \frac{6e^2a_0^5}{R^6}$$

Combining the result of Problem 11.15 we may write $E_0 - 8e^2a_0^5/R^6 <$ Ground State Energy $< E_0 - 6e^2a_0^5/R^6$.

CHAPTER THIRTEEN

The WKB Approximation

13.1. Introduction

As has already been mentioned, the exact solution of the Schrödinger equation can be obtained only for a few potential energy variations. In many cases, the Hamiltonian can be written as a sum of two parts ($H = H_0 + H'$) where the energy eigenvalues and the corresponding eigenfunctions are known and the effect of H' can be assumed to be small. In such cases one can develop the perturbation method which has been discussed in Chapter 11. Although the use of first order perturbation theory is fairly straightforward, the use of second order results is very cumbersome as it involves a summation over an infinite number of states [see Eq. (24) of Chapter 11]. On the other hand, the variational method (see Chapter 12) can give extremely good estimate of the ground state energy by choosing an appropriate trial function. The method, however, becomes quite cumbersome when one has to apply to higher excited states.

In this chapter we will develop yet another approximate method which gives a direct solution of the Schrödinger equation. The method, which is usually referred to as the WKB (Wentzel-Kramers-Brillouin) method, is applicable to potentials which are such that the Schrödinger equation is separable to one-dimensional equations; further, the potential should be *slowly varying* such that

$$\left| \frac{1}{k(x)} \frac{dk}{dx} \right| \ll k \tag{1}$$

where

$$k(x) = \frac{1}{\hbar}\, p(x) = \left[\frac{2m}{\hbar^2}(E - V(x)) \right]^{1/2} \tag{2}$$

represents the local wave number*. It is of interest to mention that the motion of a particle in a varying potential is analogous to the behaviour of light in a medium of varying refractive index. If the refractive index changes rapidly, one has reflections; if the change is gradual, the trajectory is not straight but there are practically no reflections. The behaviour of a particle is quite similar. The condition for no reflection is that the change in wavelength over a wavelength is small compared to the wavelength, i.e.,

$$\left| \frac{\partial \lambda}{\partial x}\, \lambda \right| \ll \lambda \tag{3}$$

---

* We may point out that it is sometimes possible to modify the WKB method, so it applicable to abruptly changing potential energy variations (see Sec. 13.3.1).

In terms of the local wave number $k(x)$, defined through the equation

$$k(x) = \frac{2\pi}{\lambda(x)} \tag{4}$$

one obtains the condition given by Eq. (1).

In Sec. 13.2, we obtain the WKB solutions of the one dimensional Schrödinger equation. In Sec. 13.3, these solutions are used to derive the quantization condition which determines the energy eigenvalues corresponding to bound state problems. In Sec. 13.3 we show that the quantization condition (obtained by using the WKB method) is closely related to the Bohr-Sommerfeld quantization conditions of the 'old quantum theory'. In Sec. 13.4 we use the WKB solutions to study the barrier penetration problem and obtain an approximate expression for tunnelling probability. In Sec. 13.5 the use of the WKB method in problems involving a spherically symmetric potential has been discussed. In Sec. 13.6 the connection formulae are derived.

13.2. The WKB Method for One Dimensional Problems

The one dimensional Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0 \tag{5}$$

which for $V(x) < E$ can be written in the form

$$\frac{d^2\psi}{dx^2} + k^2(x)\psi(x) = 0 \tag{6}$$

where $k(x)$ is given by the Eq. (2). If $k(x)$ is a constant (i.e., independent of x), the solution of Eq. (6) is of the form $\exp(\pm ikx)$, which suggests that when $k(x)$ is slowly varying one may try a solution of the form

$$\psi(x) = e^{iu(x)}$$

If we substitute this in Eq. (6) and neglect the term involving d^2u/dx^2, we would readily obtain

$$u(x) = \pm \int^x k(x)dx$$

Thus the *zeroeth order* solution of Eq. (6) is of the form

$$\psi_0(x) = \exp\left[\pm i\int^x k(x)dx\right] \tag{7}$$

Indeed, if we differentiate $\psi_0(x)$, we would obtain

$$\frac{d^2\psi_0}{dx^2} + \left[k^2(x) \mp \tfrac{1}{2} i \frac{dk}{dx}\right]\psi_0(x) = 0$$

Thus if the term on the right hand side is negligible [which will indeed be the case when Eq. (1) is satisfied] then $\psi_0(x)$ is indeed an accurate solution of Eq. (6). In order to obtain a better solution we write

$$\psi(x) = F(x)\psi_0(x)$$

If we substitute this in Eq. (6) and neglect the term involving d^2F/dx^2, we obtain

$$\frac{1}{F}\frac{dF}{dx} = \frac{1}{2k(x)}\frac{dk(x)}{dx}$$

the solution of which is

$$F(x) = \frac{1}{\sqrt{k(x)}}$$

The solutions

$$\psi(x) = \frac{1}{\sqrt{k(x)}}\, e^{\pm i\int k(x)\,dx} \tag{8}$$

are known as the WKB solutions. The most general WKB solution is the linear combination

$$\psi(x) = \frac{C_1}{\sqrt{k}}\, e^{i\int k(x)\,dx} + \frac{C_2}{\sqrt{k}}\, e^{-i\int k(x)\,dx} \tag{9}$$

Similarly when $V(x) > E$, the Schrödinger equation can be written in the form

$$\frac{d^2\psi}{dx^2} - \kappa^2(x)\,\psi(x) = 0 \tag{10}$$

where

$$\kappa(x) = \left[\frac{2m}{\hbar^2}\,(V(x) - E)\right]^{1/2} \tag{11}$$

The WKB solution of Eq. (10) is

$$\psi(x) = \frac{D_1}{\sqrt{\kappa}}\, e^{\int^x \kappa(x)\,dx} + \frac{D_2}{\sqrt{\kappa}}\, e^{-\int^x \kappa(x)\,dx} \tag{12}$$

The WKB solutions are valid when Eq. (1) and a similar equation for $\kappa(x)$ are satisfied. Obviously, the WKB solutions will never be valid when $V(x)$ is close to E. In Fig. 13.1 we have plotted typical variations of $V(x)$ with x; the horizontal arrow represents the value of E. The point $x = a$, where

$$V(x)\big|_{x=a} = E \tag{13}$$

is known as the turning point.* The WKB solutions are not valid near $x = a$; however, the WKB approximation gives solutions for $x \ll a$ [Eq. (9)] and for $x \gg a$ [Eq. (12)]. The question is how to match solutions of the two regions $x \ll a$ and $x \gg a$; we call them regions I and II (see Fig. 13.1). In order to match the solutions, we consider the behaviour of the wavefunction near the turning point $x = a$. We assume that in the neighbourhood of the turning point, the potential energy variation is approximately linear; i.e., near $x = a$ we may write

$$\frac{2m}{\hbar^2}\Big[E - V(x)\Big] \simeq -\alpha(x-a) \tag{14}$$

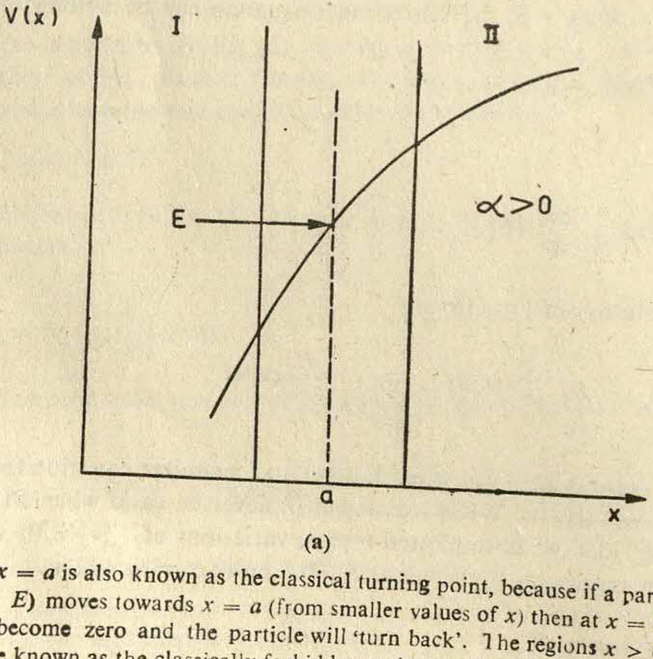
Near the turning point, if $V(x)$ is an increasing function of x [see Fig. 13.1(a)], α would be positive; conversely, if $V(x)$ is a decreasing function of x [see Fig. 13.1(b)], α would be negative. Substituting Eq. (14) in the Schrödinger equation (Eq. 5) we get

$$\frac{d^2\psi}{dx^2} - \alpha(x-a)\,\psi(x) = 0 \tag{15}$$

The solution of the above equation can be obtained in terms of Airy functions; using their asymptotic forms it is possible to obtain the connection between the WKB solutions. The details are worked out in Sec. 13.6, we give the results here :

Case I : $\alpha > 0$ [Barrier to the right—see Fig. 13.1(a)] :

$$\frac{2}{\sqrt{k}}\sin\left[\int_x^a k(x)\,dx + \frac{\pi}{4}\right] \longleftrightarrow \frac{1}{\sqrt{\kappa}}\exp\left[-\int_a^x \kappa(x)\,dx\right] \tag{16}$$



(a)

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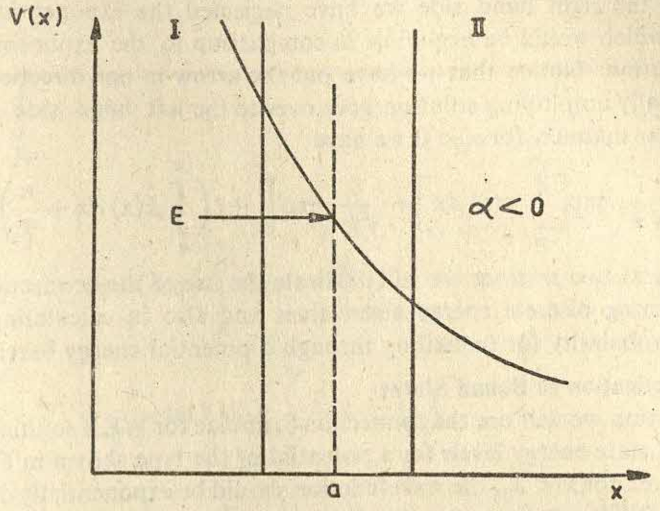
*The point $x = a$ is also known as the classical turning point, because if a particle (having a total energy E) moves towards $x = a$ (from smaller values of x) then at $x = a$ the kinetic energy would become zero and the particle will 'turn back'. The regions $x > a$ and $x < a$ (in Fig. 13.1) are known as the classically forbidden region and the classically allowed region respectively.



(b)

Fig. 13.1 A smooth potential energy variation. The point $x = a$ where $V(x) = E$ is known as the turning point.

$$\frac{1}{\sqrt{k}}\cos\left[\int_x^a k(x)\,dx+\frac{\pi}{4}\right]\longleftarrow\!\!\gg\frac{1}{\sqrt{\kappa}}\exp\left[\int_a^x \kappa(x)\,dx\right] \tag{17}$$

Case II : $\alpha < 0$ [Barrier to the left—see Fig. 13.1 (b)]

$$\frac{1}{\sqrt{\kappa}}\exp\left[-\int_x^a \kappa(x)\,dx\right]\longleftarrow\!\!\gg\frac{2}{\sqrt{k}}\sin\left[\int_a^x k(x)\,dx+\frac{\pi}{4}\right] \tag{18}$$

$$\frac{1}{\sqrt{\kappa}}\exp\left[+\int_x^a \kappa(x)\,dx\right]\ll\!\!\longrightarrow\frac{1}{\sqrt{k}}\cos\left[\int_a^x k(x)\,dx+\frac{\pi}{4}\right] \tag{19}$$

The above four equations are known as the 'connection formulae'; these formulae tell us how the WKB solutions on one side of the turning point go over to the WKB solutions on the other side of the turning point. The expressions on the left and right hand sides of the connection formulae represent respectively the WKB solutions in the regions far to the left and far to the right of the turning point. The double arrow represents the direction along which the connection formulae are strictly valid; this point is discussed in detail in Sec. 13.6. If we multiply Eq. (16) by $\pm i$ and add to Eq. (17) we get

$$\frac{1}{\sqrt{k}}\exp\left[\pm i\left(\int_x^a k(x)\,dx+\frac{\pi}{4}\right)\right]\rightarrow\frac{1}{\sqrt{\kappa}}\exp\left[\int_a^x \kappa(x)\,dx\right]\text{ for }\alpha>0 \tag{20}$$

where on the right hand side we have neglected the exponentially decaying solution which would be negligible in comparison to the exponentially amplifying solution. Notice that we have put the arrow in one direction only. The exponentially amplifying solution goes over to the left hand side of Eq. (17). In a similar manner, for $\alpha < 0$ we have

$$\frac{1}{\sqrt{\kappa}}\exp\left[\int_x^a \kappa(x)\,dx\right] \leftarrow \frac{1}{\sqrt{k}}\exp\left[\pm i\left(\int_a^x k(x)\,dx+\frac{\pi}{4}\right)\right],\ \alpha<0 \quad (21)$$

In the next two sections we will illustrate the use of the connection formulae in determining discrete energy eigenvalues and also in calculating the transmission probability for tunnelling through a potential energy barrier.

13.3 Application to Bound States

In this section we will use the connection formulae for WKB solutions to obtain the bound state energy levels for a potential of the type shown in Fig. 13.2. In region I, i.e., for $x < x_1$, the wavefunction should be exponentially decaying and hence the WKB solution must be of the form

$$\psi_I = \frac{1}{\sqrt{\kappa}}\exp\left[-\int_x^{x_1} \kappa(x)\,dx\right] \quad (22)$$

Around the turning point $x = x_1$, α is negative, therefore in region II, ψ_I would go over to (see Eq. 18)

$$\psi_{II} = \frac{2}{\sqrt{k}}\cos\left[\int_{x_1}^{x} kdx - \frac{\pi}{4}\right]$$

$$= \frac{2}{\sqrt{k}}\cos\left[\theta - \int_x^{x_2} kdx - \frac{\pi}{4}\right]$$

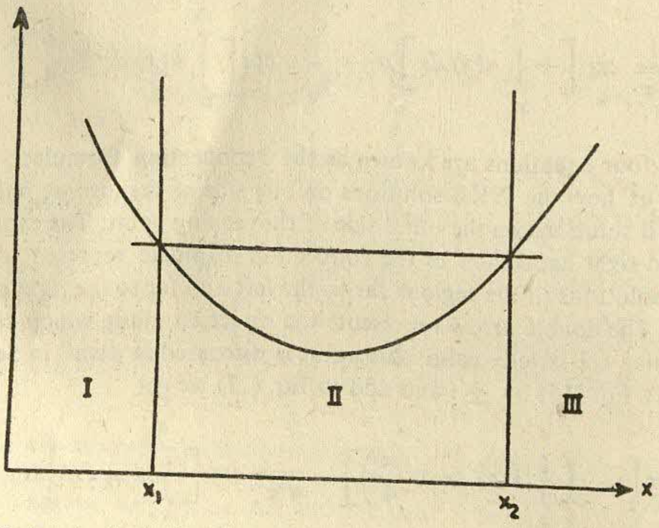


Fig. 13.2 A potential well. The points $x = x_1$ and $x=x_2$ are the turning points.

where

$$\theta = \int_{x_1}^{x_2} k(x)\, dx$$

Thus

$$\psi_{\rm II} = \frac{2}{\sqrt{k}} \cos\theta \cos\left(\int_x^{x_2} kdx + \frac{\pi}{4}\right)$$

$$+ \frac{2}{\sqrt{k}} \sin\theta \sin\left(\int_x^{x_2} kdx + \frac{\pi}{4}\right) \tag{23}$$

Equation (17) tells us that $\cos(\int_x^{x_2} kdx + \pi/4)$ will go over to an exponentially increasing solution in region III and thus, for a bound state, we must have

$$\cos\theta = 0 \tag{24}$$

or

$$\int_{x_1}^{x_2} k(x)dx = \left(\frac{2m}{\hbar^2}\right)^{1/2} \int_{x_1}^{x_2} [E - V(x)]^{1/2}\, dx = (n + \tfrac{1}{2})\pi \tag{25}$$

which is known as the quantization condition that bound states must satisfy. For a given form of $V(x)$, Eq. (25) is satisfied for certain specific values of E; these are the discrete eigenvalues corresponding to $V(x)$ in the WKB approximation (see the first six problems at the end of this chapter).

13.4 The Physical Interpretation of the Quantization condition

It is of interest to mention that in the old quantum theory* only those stationary states are allowed for which the following condition is satisfied

$$\oint pdx = nh; \quad n = 0, 1, 2, 3, \ldots \tag{26}$$

where we have restricted ourselves to motion in one dimension. Equation (26) is known as the Sommerfeld quantization condition and the left hand side is the *Sommerfeld phase integral* taken over a complete classical oscillation. Since $p = \hbar k$, Eq. (26) can also be written in the form

$$\oint kdx = 2n\pi; \quad n = 0, 1, 2, \ldots \tag{27}$$

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*See, e.g., Pauling and Wilson (1935).

Now $\oint kdx$ represents the total phase change in one complete oscillation and is therefore given by

$$\oint kdx = 2\int_{x_1}^{x_2} kdx + \varphi_1 + \varphi_2 \tag{28}$$

where φ_1 and φ_2 are the 'abrupt' phase shifts that occur at the turning points x_1 and x_2. Thus, we have

$$\int_{x_1}^{x_2} kdx = n\pi - \tfrac{1}{2}(\varphi_1 + \varphi_2) \tag{29}$$

We now consider two cases.

Case I

The first case corresponds to the $V(x)$ variation such that there is no discontinuity in $V(x)$ at the turning points (e.g., Fig. 13.2). For such a case

$$\varphi_1 = \varphi_2 = -\frac{\pi}{2} \tag{30}$$

This immediately follows from the right hand side of Eq. (18) which can be written in the form

$$\frac{2}{\sqrt{k}}\ \frac{1}{2}e^{i\pi/4}\left[e^{-i\int k(x)dx} + e^{-i(\pi/2)}e^{+i\int^{x} k(x)dx}\right] \tag{31}$$

Since the first term represents the incident wave (from the right) and the second the reflected wave, we see that there is an 'abrupt' phase shift of $-\pi/2$ on

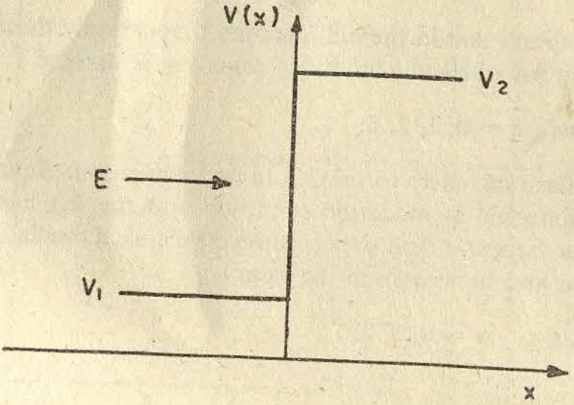

Fig. 13.3 A potential step at $x = 0$. A particle with energy E is incident from the left.

reflection. Thus Eq. (29) becomes

$$\int_{x_1}^{x_2} k(x)dx = (n + \tfrac{1}{2})\,\pi \tag{32}$$

which is identical to Eq. (25).

Case II

When there is an abrupt change in the value of $V(x)$ at one or both the caustics, then using a method similar to that used in Sec. 4.2 it is easy to show that the phase change on reflection by a potential step of the type shown in Fig 13.3 is given by (cf. Eq. 14 of Chapter 4)

$$\varphi = -\,2\tan^{-1}\left(\frac{V_2 - E}{E - V_1}\right)^{1/2} \tag{33}$$

As an example, we consider the square well potential shown in Fig. 13.4. We have

$$\varphi_1 = \varphi_2 = -\,2\tan^{-1}\sqrt{\frac{V_0 - E}{E}} \tag{34}$$

Thus Eq. (29) becomes

$$-\left(\frac{V_0 - E}{E}\right)^{1/2} = \tan\left(\frac{n\pi}{2} - \frac{ka}{2}\right) \tag{35}$$

which gives the exact results [cf. Eqs. (43) and (44) (of Chapter 3]; $n = 0, 2, 4, \ldots$ correspond to the symmetrical solutions and $n = 1, 3, 5, \ldots$ correspond to anti-symmetrical solutions.

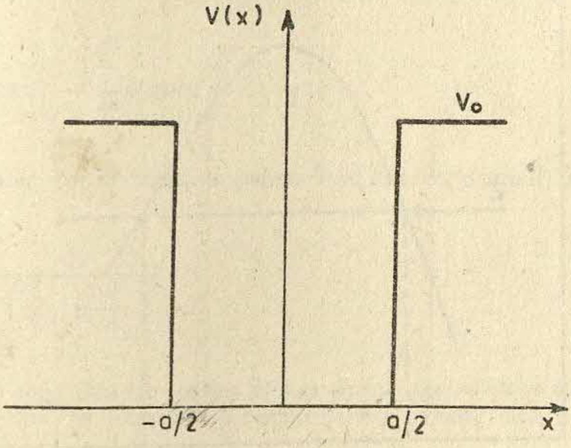

Fig. 13.4 The square well potential.

13.4. Application to Barrier Penetration

We next consider a potential of the type shown in Fig. 13.5. We assume that a wave is incident from the left. Thus, in region I, there will be an incident as well as a reflected wave. On the other hand, in region III there will only be an outgoing wave. Our objective is to calculate the transmission coefficient for a given value of E. Since in region III there is only an outgoing wave, the WKB solution in this region will be of the form

$$\psi_{\text{III}} = \frac{F}{\sqrt{k(x)}} \exp\left(i \int_b^x k(x)dx \right) \tag{36}$$

Using the connection formula given by Eq. (21), we have the following WKB solution in region II.

$$\psi_{\text{II}} = \frac{F}{\sqrt{\kappa}} e^{-i\pi/4}\, e^{\int_x^b \kappa\, dx}$$

$$= \left[F e^{-i\pi/4} e^{\int_a^b \kappa\, dx} \right] \frac{1}{\sqrt{\kappa(x)}}\, e^{-\int_a^x \kappa\, dx} \tag{37}$$

In order to obtain the solution in region I, we use the connection formula given by Eq. (41) to obtain

$$\psi_{\text{I}} = \left[F e^{-i\pi/4} e^{\int_a^b \kappa(x)dx} \right] \frac{2}{\sqrt{k}} \cos\left[\int_x^a k(x)dx - \frac{\pi}{4} \right] \tag{38}$$

or $$\psi_{\text{I}} = \psi_{\text{inc}} + \psi_{\text{refl}} \tag{39}$$

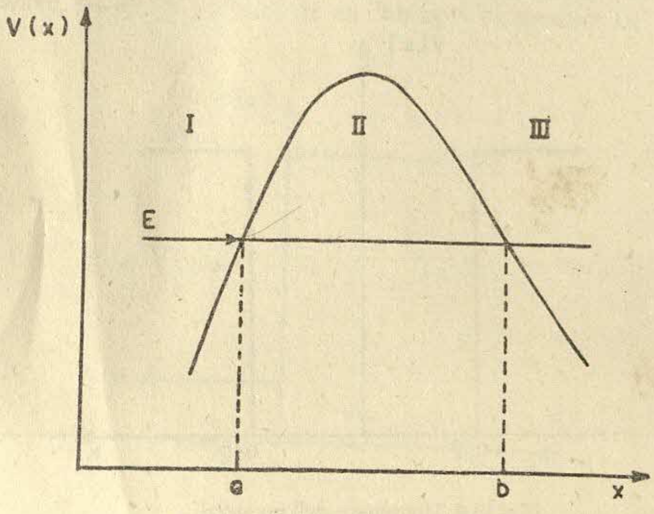

Fig. 13.5 A potential barrier. The points $x = a$ and $x = b$ are the turning points.

where $$\psi = \frac{A}{\sqrt{k}} e^{-i\int_x^a k(x)dx} \tag{40}$$

and $$\psi_{\text{refl}} = \frac{B}{\sqrt{k}} e^{+i\int_x^a k(x)dx} \tag{41}$$

represent the wavefunctions corresponding to the incident and reflected waves respectively; further,

$$A = F \exp\left[\int_a^b \kappa(x)dx\right] \tag{42}$$

and

$$B = Fe^{-i\pi/2} \exp\left[\int_a^b \kappa(x)dx\right] \tag{43}$$

implying that the reflected wave has the same amplitude* with a phase change of $\pi/2$.

The currents can easily be calculated by using the relation [see Eq. (36) of Chapter 2]

$$J = \text{Real part of}\left[\psi^* \frac{\hbar}{im} \frac{d\psi}{dx}\right] \tag{44}$$

and one obtains the following expression for the transmission coefficient

$$T = \left|\frac{F}{A}\right|^2 = \theta^2 \tag{45}$$

where

$$\theta = \exp\left[-\int_a^b \kappa(x)dx\right] \tag{46}$$

A slightly better approximation (when θ is not very small) is (see Problem 13.15)

$$T = \frac{1}{\left(\frac{1}{\theta} + \frac{\theta}{4}\right)^2} \tag{47}$$

---

*Thus, in the approximation scheme of this section, the reflection coefficient is unity; hence the result for the transmission coefficient will be valid when its value is extremely small; i.e., $\exp\left(-\int_a^b \kappa\, dx\right) \ll 1$ —see Eq. (47).

and consistent with this approximation, the reflection coefficient is given by (Notice that $R + T = 1$)

$$R = \frac{\left(\frac{1}{\theta} - \frac{\theta}{4}\right)^2}{\left(\frac{1}{\theta} + \frac{\theta}{4}\right)^2} \tag{48}$$

13.5 The WKB Method for Three Dimensional Problems

The radial equation for a particle in a central field is given by [see Eq. (21) of Chapter 5]

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right]u(r) = 0 \tag{49}$$

where $u(r) = rR(r)$. Since r goes from 0 to ∞, it is appropriate that we change the independent variable in the radial equation to x so that $r = 0$ corresponds to $x = -\infty$. In order to do this, we introduce the transformation

$$r = e^x$$

The function u then satisfies

$$\frac{d^2u}{dx^2} - \frac{du}{dx} + e^{2x}\frac{2m}{\hbar^2}\left[E - V(e^x) - \frac{l(l+1)\hbar^2}{2m}e^{-2x}\right]u = 0$$

In order to bring the above equation in the one dimensional Schrödinger equation form, we introduce a new dependent variable

$$\chi(x) = u(x)\,e^{-1/2x}$$

The function $\chi(x)$ satisfies the following equation

$$\frac{d^2\chi}{dx^2} + e^{2x}\frac{2m}{\hbar^2}\left[E - V(e^x) - (l+\tfrac{1}{2})^2\frac{\hbar^2}{2m}e^{-2x}\right]\chi(x) = 0 \tag{50}$$

Thus, instead of the integral $\int^x k(x)dx$, we would have

$$\int^x\left[e^{2x}\frac{2m}{\hbar^2}\left\{E - V(e^x) - \frac{(l+\frac{1}{2})^2\hbar^2}{2m}e^{-2x}\right\}\right]^{1/2}dx = \int^r k(r)\,dr$$

where we have gone back to the original variable r and

$$k(r) = \left[\frac{2m}{\hbar^2}\left\{E - V(r) - \frac{(l+\frac{1}{2})^2\hbar^2}{2mr^2}\right\}\right]^{1/2} \tag{51}$$

Thus the WKB solution to the radial part of equation can be considered in an exactly similar manner except for the fact that $l(l+1)$ has to be replaced by

$(l+\frac{1}{2})^2$. For example, to get the bound state energies, we must solve the equation

$$\int_{r_1}^{r_2} k(r)\,dr = (n+\tfrac{1}{2})\pi \tag{52}$$

where r_1 and r_2 are the turning points where $k(r)$ vanishes (see, e.g., Problem 13.7).

The WKB method can also be used for the approximate calculation of phase shifts in scattering theory (see Chapter 19). The expressions for phase shifts are given by* [see e.g., Morse and Feshbach (1953)]:

$$\delta_l \approx \int^{\infty}\left[\frac{2m}{\hbar^2}\left\{E - V(r) - \frac{(l+\frac{1}{2})^2\hbar^2}{2mr^2}\right\}\right]^{1/2} dr - \int^{\infty}\left[\frac{2m}{\hbar^2}\left\{E - \frac{(l+\frac{1}{2})^2\hbar^2}{2mr^2}\right\}\right]^{1/2} dr \tag{53}$$

where the lower limit corresponds to the zero of the integrand. The above expression for δ_l gives good results for large phase shifts*. It may be mentioned that since Born approximation gives accurate values of phase shifts when they are small (see Chapter 19), the Born approximation and the WKB method combined should give good estimate for δ_l for all l!

13.6 Derivation of the Connection Formulae

We return to Eq. (15)

$$\frac{d^2\psi}{dx^2} - \alpha(x-a)\,\psi(x) = 0$$

We will assume α to be positive. The above equation can be written in the form

$$\frac{d^2\psi}{dz^2} - z\psi(z) = 0 \tag{54}$$

where

$$z = \alpha^{1/3}(x-a)$$

A convenient pair of linearly independent solutions are the Airy functions $Ai(z)$ and $Bi(z)$; these functions are related to Bessel functions (see Sec. 13.6.1) and can be expressed as a series for all values of z (see Problem 13.22). However, we are interested in large values of z (both positive and negative); we have for these (see Appendices H and K) :

---

*Comparison of some calculations of exact phase shifts with those obtained by using WKB method has been made by Mott and Massey (1949), Chapter X.

$$\left.\begin{aligned} Ai(z) &\sim \frac{1}{2\sqrt{\pi}}\, z^{-1/4} e^{-\xi}, && z \to +\infty \\ &\sim \frac{1}{\sqrt{\pi}}\, |z|^{-1/4} \sin\left(\xi + \frac{\pi}{4}\right), && z \to -\infty \end{aligned}\right\} \tag{55}$$

and

$$\left.\begin{aligned} Bi(z) &\sim \frac{1}{\sqrt{\pi}}\, z^{-1/4} e^{\xi}, && z \to +\infty \\ &\sim \frac{1}{\sqrt{\pi}}\, |z|^{-1/4} \cos\left(\xi + \frac{\pi}{4}\right), && z \to -\infty \end{aligned}\right\} \tag{56}$$

where

$$\xi = \tfrac{2}{3}\, |z|^{3/2} = \tfrac{2}{3}\, \alpha^{1/2}\, |x - a|^{3/2} \tag{57}$$

It may be seen that the behaviour for large positive and large negative values of z are quite different.* This is understandable because we expect the solutions to exhibit exponential behaviour for positive z and oscillatory behaviour for negative z. That the behaviour should be such is obvious from the WKB solutions (see Eqs. 9 and 11) because for $z > 0$ Eq. (54) is simliar to Eq. (10) with $\kappa^2 = z$ giving the following as WKB solutions (see Eq. 12)

$$\psi(z) \sim \frac{1}{\sqrt{\kappa}} \exp\left[\pm \int^{x} \kappa(x)\, dx\right] = z^{1/4} \exp\left[\pm \int^{z} z^{1/2}\, dz\right]$$

$$\sim z^{1/4} e^{\pm\xi} \qquad \text{where } \xi = \tfrac{2}{3} z^{3/2}$$

Similarly $z < 0$, Eq. (54) is similar to Eq. (6) with $k^2(z) = -z = |z|$ giving the following as WKB solutions (see Eq. 9)

$$\psi(z) \sim \frac{1}{\sqrt{k}} \exp\left[\pm i \int k(x)\, dx\right] = |z|^{1/4} \exp(\pm i\xi)$$

the linear combinations of which will give the trigonometric functions.

Now, the general solution of Eq. (54) will be :

$$\psi(z) = a\, Ai(z) + b\, B_i(z)$$

---

*It should be mentioned that the right hand sides of Eqs. (18)-(21) represent the first term of what is known as the asymptotic series (see Appendices K and L); these series are in inverse powers of ξ (i.e., ξ^{-k}), they are all divergent for any finite value of ξ (or, of $|z|$) no matter how large it is. Nevertheless, they are most useful since, for large ξ, a few terms (in our case, the first terms alone) of the series will give a sufficiently precise value for the functions; taking a large number of terms will, in general, give a poorer approximation (see Appendix K).

where a and b are constants to be determined from boundary conditions. For large positive z, the first term is exponentially decreasing (see Eq. 55) and hence is negligible in comparison to the second term which is exponentially increasing (see Eq. 57). Indeed, the first term will generally be negligible compared to the second term and there is no sense in retaining it unless, for given boundary conditions, it turns out that there is no large term; i.e., $b = 0$. When this is the case (i.e., when $b = 0$)

$$\psi(z) = a\,Ai(z)$$

$$\rightarrow \frac{a}{2\sqrt{\pi}} z^{-1/4} e^{-\xi} \qquad \text{for} \quad x \rightarrow +\infty$$

$$\rightarrow \frac{a}{\sqrt{\pi}} |z|^{-1/4} \sin\left(\xi + \frac{\pi}{4}\right) \quad \text{for} \quad x \rightarrow -\infty$$

i.e., the solution

$$\frac{1}{2} z^{-1/4} e^{-\xi} \rightarrow |z|^{-1/4} \sin\left(\xi + \frac{\pi}{4}\right) \tag{58}$$

(Read the arrow as 'goes over to'). The direction of the arrow implies that it is the exponentially decaying solution in region II which goes over to the right hand side expression in region I (see Fig. 13.1*a*), the converse being not necessarily true because a small change in the phase of the sine term will give rise to a term proportional to $\cos(\xi + \pi/4)$ which would give rise to an exponentially growing term e^{ξ} (see Eq. 57 and 58). This exponentially growing term, for sufficiently large values of ξ, will inevitably be dominant over the exponentially decreasing term $e^{-\xi}$, even if the $e^{-\xi}$ term is important for smaller values of ξ. In fact, we expect the linear combination

$$\cos\varphi\, Bi(z) + \sin\varphi\, Ai(z)$$

which tends to

$$\frac{1}{\sqrt{\pi}} |z|^{-1/4} \left[\cos\varphi \cos\left(\xi + \frac{\pi}{4}\right) + \sin\varphi \sin\left(\xi + \frac{\pi}{4}\right)\right] \qquad \text{for} \quad z \rightarrow -\infty$$

to go over to

$$\frac{1}{\sqrt{\pi}} z^{-1/4}[\cos e^{\xi} + \sin\varphi\, e^{-\xi}] \qquad \text{for} \quad z \rightarrow +\infty$$

For values of φ such that $\cos\varphi$ differ appreciably from zero, the term proportional to $e^{-\xi}$ can be neglected and one has the connection formula

$$|z|^{-1/4} \frac{1}{\cos\varphi} \cos\left(\xi + \frac{\pi}{4} - \varphi\right) \rightarrow z^{-1/4} e^{\xi} \tag{59}$$

The arrow indicates that the left hand solution in region I goes over to the exponentially amplifying solution in region II; once again, the converse is not necessarily true because the neglected exponentially decaying term would alter the phase of the cosine term. This also follows from the arbitrariness of φ. In fact, we could have considered the linear combination

$$Bi(z) \pm i\, Ai(z)$$

to obtain the connection formula

$$|z^-|^{1/4} \exp\left[\pm i\left(\xi + \frac{\pi}{4}\right)\right] \rightarrow z^{-1/4} e^{\xi} \tag{60}$$

However, the connection formula (59) with $\varphi = 0$, i.e.,

$$|z|^{-1/4} \cos\left(\xi + \frac{\pi}{4}\right) \rightarrow z^{-1/4} e^{\xi} \tag{61}$$

and Eq. (58) written in the form

$$2\,|z|^{-1/4} \sin\left(\xi + \frac{\pi}{4}\right) \leftarrow z^{-1/4} e^{-\xi} \tag{62}$$

are currently used in literature. In Eqs. (61) and (62) the quantities on the LHS and RHS correspond to regions I and II respectivley.

Now, for $V(x)$ varying linearly with x (see Eq. 14), we have for $x < a$

$$k^2(x) \equiv \frac{2m}{\hbar^2}[E - V(x)] = \alpha(a - x) = \alpha^{2/3}\,|z|$$

giving

$$\int_x^a k(x)\,dx = \alpha^{1/2} \int_x^a \left(a - x\right)^{1/2} dx = \frac{2}{3}\left(-z\right)^{3/2} = \xi$$

Similarly for $x > a$

$$\kappa^2(x) = \frac{2m}{\hbar^2}[V(x) - E] \approx \alpha(x - a)\, \alpha^{2/3} z$$

giving

$$\int_a^x \kappa(x)\,dx = \alpha^{1/2} \int_a^x (x - a)^{1/2}\,dx = \frac{2}{3}\, z^{3/2} = \xi$$

Thus we have the following connection formulae :

$$\frac{1}{\sqrt{k}} \cos\left(\int_x^a k(x)\,dx + \frac{\pi}{4}\right) \rightarrow \frac{1}{\sqrt{\kappa}} \exp\left(\int_a^x \kappa(x)\,dx\right) \tag{63}$$

$$\frac{2}{\sqrt{k}} \sin\left(\int_x^a k(x)\,dx + \frac{\pi}{4}\right) \leftarrow \frac{1}{\sqrt{\kappa}} \exp\left(-\int_a^x \kappa(x)\,dx\right) \tag{64}$$

We also have

$$\frac{1}{\sqrt{k}} \exp\left[\pm i \left\{ \int_x^a k(x)\, dx + \frac{\pi}{4} \right\}\right] \rightarrow \frac{1}{\sqrt{\kappa}} \exp\left(\int_a^x \kappa(x)\, dx \right)$$

These are the connection formulae which were written down in Sec. 13.2 [see Eqs. (16) and (17)]. In an exactly similar manner we can derive the connection formulae for $\alpha < 0$ [see Eqs. (18) and (19)].

It is of interest to mention here that strictly speaking, the connection formulae should be used only along the direction of the arrow as has been discussed above. However, in literature, the connection formulae, Eqs. (63) and (64) have been used in the reverse direction also, i.e., along the direction opposite to that of the arrow. Pauli (1958) has argued on the validity of the connection formulae [Eqs. (63) and (64)] on the basis of conservation of current density which suggests the validity of the connection formulae in the reverse direction also. In fact he writes the following as the 'correct' connection :

$$\psi(x) = \frac{C}{\sqrt{k(x)}} \exp\left[i \left(\int^{a} k(x)\, dx - \frac{\pi}{4} \right)\right] \qquad \text{for } x < a \qquad (65)$$

$$= \frac{C}{i\sqrt{\kappa}} \exp\left[\int_a^x \kappa(x)\, dx \right] + \frac{C}{2\sqrt{\kappa}} \exp\left[- \int^x \kappa(x)\, dx \right]$$

$$\text{for } x > a \qquad (66)$$

Notice that equating the real and imaginary parts, we get Eqs. (64) and (63) respectively. Reference may also be made to Heading (1962) where the use of connection formulae in both directions has been justified. On the other hand, many authors have argued that the use of these formulae in the reverse direction is not correct (see, e.g., Froman and Froman, 1965). Nevertheless, in literature, the connection formulae have been extensively used in the reverse direction (see, e.g., Problems 5, 6, 15, 16, 17 and 18 of this chapter) and indeed in Problem 13.6 we find that the WKB results compare very well with the exact results.

13.6.1 RELATIONSHIP BETWEEN AIRY AND BESSEL FUNCTIONS

We start with Eq. (54)

$$\frac{d^2\psi}{dz^2} - z\psi(z) = 0$$

We first consider the region $z > 0$. We make the transformation

$$\psi(z) = z^{1/2}\, \phi(z)$$

On substitution we find that $\phi(z)$ satisfies the differential equation

$$z^2 \frac{d^2\phi}{dz^2} + z \frac{d\phi}{dz} - \left[z^3 + \frac{1}{4} \right] \phi(z) = 0$$

We make another transformation

$$\xi = \tfrac{2}{3} z^{3/2}$$

to obtain

$$\xi^2 \frac{d^2\phi}{d\xi^2} + \xi \frac{d\phi}{d\xi} - \left[\xi^2 + \frac{1}{9}\right] \phi(\xi) = 0 \tag{67}$$

which is known as the modified Bessel equation (see Appendix H). The solutions are $I_{1/3}(\xi)$ and $I_{-1/3}(\xi)$. Thus the solutions of Eq. (54) for $z > 0$ are given by

$$\psi(z) = z^{1/2}\, I_{\pm 1/3}(\xi) \tag{68}$$

For $z < 0$, we should write $\eta = -z$ to obtain

$$\frac{d^2\psi}{d\eta^2} + \eta\, \psi(\eta) = 0$$

We proceed in an exactly similar manner : we make the transformations $\psi(\eta) = \eta^{1/2} \phi(\eta)$ and $\zeta = \tfrac{2}{3}\eta^{3/2}$ to obtain

$$\zeta^2 \frac{d^2\phi}{d\zeta^2} + \zeta \frac{d\phi}{d\zeta} + \left[\zeta^2 - \frac{1}{9}\right] \phi(\zeta) = 0 \tag{69}$$

which is the Bessel equation (see Appendix H) and the solutions are $J_{\pm 1/3}(\zeta)$. Thus, the general solution of Eq. (54) may be written as

$$\begin{aligned} \psi(z) &= z^{1/2}[C_1 I_{-1/3}(\xi) + C_2 I_{1/3}(\xi)] && \text{for } z > 0 \\ &= |z|^{1/2}[C_3 J_{-1/3}(\xi) + C_4 J_{1/3}(\xi)] && \text{for } z < 0 \end{aligned} \tag{70}$$

where

$$\xi = \tfrac{2}{3} |z|^{3/2}$$

It may be noted that if we make the transformation $\zeta = i\xi$ in Eq. (67) we would get Eq. (69). Thus $I_n(\xi)$ should be proportional to $J_n(i\xi)$; indeed one writes

$$I_n(\xi) = i^{-n} J_n(i\xi) = \sum_{r=0}^{\infty} \frac{(\xi/2)^{n+2r}}{r!\,\Gamma(n+r+1)} \tag{71}$$

where we have used the relation

$$J_n(\xi) = \sum_{r=0}^{\infty} (-1)^r \frac{(\xi/2)^{n+2r}}{r!\,\Gamma(n+r+1)} \tag{72}$$

In Eq. (70), for given value of C_1 and C_2, C_3 and C_4 are determined from the condition that $\psi(z)$ and $d\psi/dz$ should be continuous at $z = 0$. A pair of independent solutions (which along with their derivatives are continuous at $z = 0$)

are the Airy functions defined through the following equations

$$\left.\begin{aligned} Ai(z) &= \tfrac{1}{3}(z)^{1/2}[I_{-1/3}(\xi) - I_{1/3}(\xi)], & z > 0 \\ &= \tfrac{1}{3}\,|z|^{1/2}[J_{-1/3}(\xi) + J_{1/3}(\xi)], & z < 0 \\ Bi(z) &= \frac{1}{\sqrt{3}}\, z^{1/2}[I_{-1/3}(\xi) + I_{1/3}(\xi)], & z > 0 \\ &= \frac{1}{\sqrt{3}}\,|z|^{1/2}[J_{-1/3}(\xi) - J_{-1/3}(\xi)], & z < 0 \end{aligned}\right\} \tag{73}$$

The continuity of these functions and their derivatives are discussed in Problems 13.21 and 13.22. The main reason for choosing the above equations is because of their convenient asymptotic forms as given by Eq. (55) and (56). The functions are plotted in Fig. 13.6. Notice that the exponentially decaying solution in the region $z > 0$ goes over to the solution proportional to $|z|^{1/4} \sin(\xi + \pi/4)$ in the region $z < 0$ which gives the connection formula given by Eq. (62). Similarly, the other connection formulae can be derived.

In order to derive the asymptotic forms of the Airy functions we start with the asymptotic forms of the Bessel functions (see Appendix H)

$$J_n(\xi) \underset{\xi \to \infty}{\rightarrow} \left(\frac{2}{\pi\xi}\right)^{1/2} \cos\left[\xi - \frac{n\pi}{2} - \frac{\pi}{4}\right] \tag{74}$$

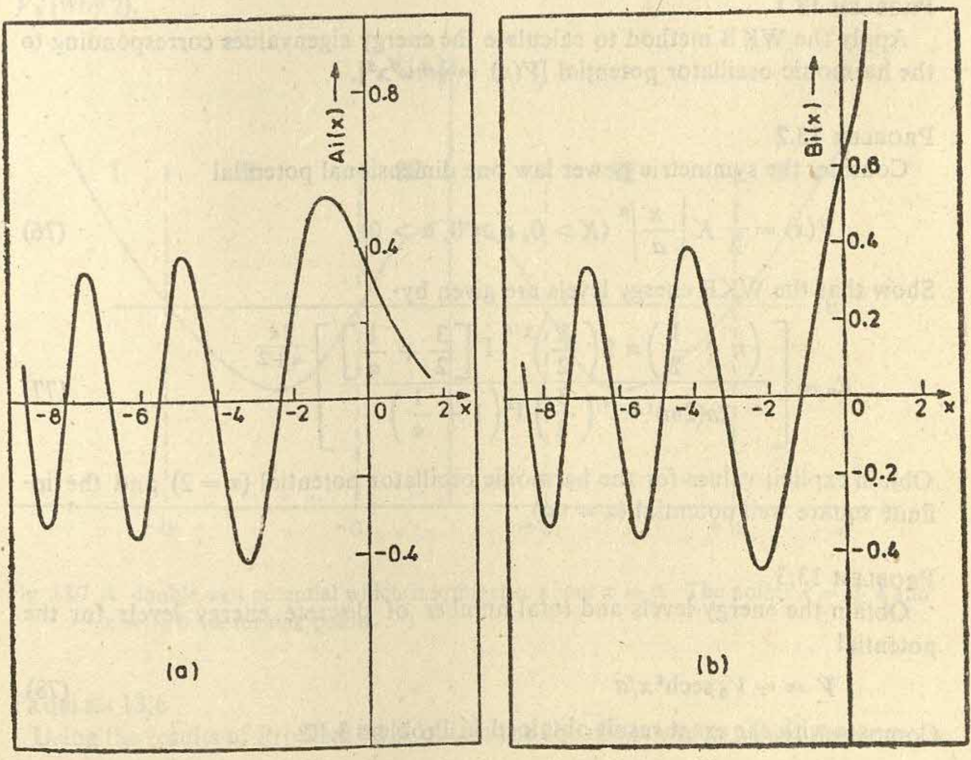

Fig. 13.6 The variations of $Ai(x)$ and $Bi(x)$ with x.

Thus

$$I_n(\xi) \underset{\xi\to\infty}{\rightarrow} i^{-n}\left(\frac{2}{\pi i\xi}\right)^{1/2}\left[\frac{e^{i(i\xi-n\pi/2-\pi/4)}+e^{-i(i\xi-n\pi/2-\pi/4)}}{2}\right]$$

Since $i = e^{i\pi/2}$, we get after simplification

$$I_n(\xi) \underset{\xi\to\infty}{\rightarrow} \left(\frac{1}{2\pi\xi}\right)^{1/2}[e^{\xi}+e^{-i\pi(n+1/2)}e^{-\xi}] \tag{75}$$

It would seem that it is meaningless to keep the $e^{-\xi}$ term because the exponentially increasing term e^{ξ} will always dominate over the exponentially decreasing term; however, it is necessary to retain the decreasing term for calculating the asymptotic form of $Ai(z)$. Indeed if we substitute the above asymptotic forms in Eq. (73) we would get Eqs. (55) and (56). Notice that although the asymptotic forms of both $I_{1/3}(\xi)$ and $I_{-1/3}(\xi)$ are exponentially increasing, the asymptotic forms of $Ai(z)$ and $Bi(z)$ are exponentially decreasing and exponentially increasing repectively. The case is similar to the solutions cosh x and sinh x of the differential equation $d^2\psi/dx^2 - \psi = 0$, both solutions diverging as $x \to \infty$; however, in most cases it is more convenient to choose e^{x} and e^{-x} as solutions which are of course linear combinations of cosh x and sinh x.

PROBLEMS

PROBLEM 13.1

Apply the WKB method to calculate the energy eigenvalues corresponding to the harmonic oscillator potential $[V(x) = \frac{1}{2}m\omega^2x^2]$.

PROBLEM 13.2

Consider the symmetric power law one dimensional potential

$$V(x) = \frac{1}{2}K\left|\frac{x}{a}\right|^{\alpha} \quad (K>0,\ a>0,\ \alpha>0) \tag{76}$$

Show that the WKB energy levels are given by

$$E_n = \left[\frac{\left(n+\frac{1}{2}\right)\pi\hbar\left(\frac{K}{2}\right)^{1/\alpha}\Gamma\left[\frac{3}{2}+\frac{1}{\alpha}\right]}{2a(2m)^{1/2}\,\Gamma\left(\frac{3}{2}\right)\Gamma\left(1+\frac{1}{\alpha}\right)}\right]^{\frac{2\alpha}{\alpha+2}} \tag{77}$$

Obtain explicit values for the harmonic oscillator potential ($\alpha = 2$) and the infinite square well potential ($\alpha = \infty$).

PROBLEM 13.3

Obtain the energy levels and total number of discrete energy levels for the potential

$$V = -V_0\,\mathrm{sech}^2\,x/a \tag{78}$$

Compare with the exact result obtained in Problem 3.12.

PROBLEM 13.4

Show that the WKB energy levels corresponding to the free fall of a particle in earth's gravitational field are given by

$$E_n = \tfrac{1}{2}[9(n + \tfrac{3}{4})^2 \pi^2 m g^2 \hbar^2]^{1/3} \tag{79}$$

[*Hint* : $V(z) = mgz, \quad (z > 0)$

$\qquad\qquad = \infty \quad (z < 0)$

Use Eq. (29) with $\varphi_1 = -\pi$ [see Eq. (33) with $V_2 = \infty$] and $\varphi_2 = -\pi/2$ [see Eq. (30)]. Compare with the exact result in Problem 3.14.]

PROBLEM 13.5

Consider a double well symmetric potential as shown in Fig. 13.7. Using the WKB connection formulae, show that (for $E < V_0$) the energy eigenvalues are determined by solving the following transcendental equation

$$\cot\left[\int_{-b}^{-a} k(x)\,dx\right] = \pm\frac{1}{2}\exp\left[-\int_{-a}^{+a} \kappa(x)\,dx\right] \tag{80}$$

where the upper and lower signs correspond to symmetric and anti-symmetric solutions respectively; here $x = \pm a$ and $x = \pm b$ are the turning points. We may note that the above equation will not give accurate results for E close to V_0 (why ?).

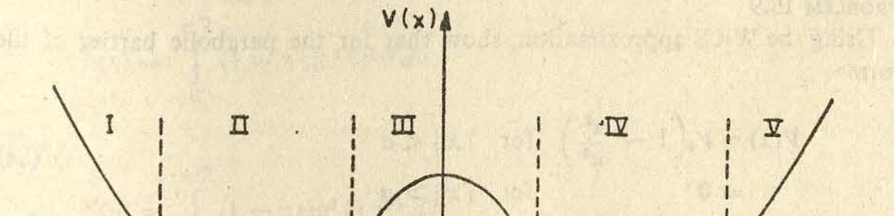

Fig. 13.7 A double well potential which is symmetric about $x = 0$. The points $x = \pm a$ and $x = \pm b$ are turning points.

PROBLEM 13.6

Using the results of Problem 13.5, obtain the equations which would determine the energy levels of the double oscillator for which (see Problem 3.15)

$$V(x) = \tfrac{1}{2}m\omega^2[|x| - a]^2 \tag{81}$$

PROBLEM 13.7

Using the WKB method, calculate the energy levels for the hydrogen atom problem, i.e., $V(r) = -Ze^2/r$.

PROBLEM 13.8

(a) Using the WKB approximation, calculate the transmission coefficient for the triangular barrier for which the potential energy variation is given by

$$\begin{aligned} V(x) &= V_0\left(1 - \frac{|x|}{a}\right), & |x| < a \\ &= 0 & |x| > a \end{aligned} \tag{82}$$

(b) Since the potential energy variation is linear, one can exactly solve the Schrödinger equation (see Problem 4.9). Show that the WKB solutions are accurate when

$$\left(\frac{2mV_0a^2}{\hbar^2}\right)^{1/2}\left(1 - \frac{E}{V_0}\right)^{3/2} \gg 1 \tag{83}$$

PROBLEM 13.9

Using the WKB approximation, show that for the parabolic barrier of the form

$$\begin{aligned} V(x) &= V_0\left(1 - \frac{x^2}{a^2}\right) & \text{for } |x| < a \\ &= 0 & \text{for } |x| > a \end{aligned} \tag{84}$$

the transmission coefficient is given by

$$T \approx \exp\left[-\pi\left(\frac{2mV_0a^2}{\hbar^2}\right)^{1/2}\left(1 - \frac{E}{V_0}\right)\right] \tag{85}$$

PROBLEM 13.10

(a) Calculate the transmission coefficient for the barrier of the form

$$\begin{aligned} V(x) &= 0 & \text{for } x < 0 \\ &= V_0 - \alpha x & \text{for } x > 0\ (\alpha > 0) \end{aligned} \tag{86}$$

(b) The above potential energy variation is applicable to the field emission of electrons from a metal surface. Then $V_0 = E_F + \phi$ and $\alpha = (-q)\mathcal{E}$ where E_F represents the Fermi energy, ϕ the work function, $q(< 0)$ the electronic charge and $\mathcal{E}$ the strength of the electric field. Assume $T = 0°\text{K}$ and calculate the dependence of the electric current on the electric field.

PROBLEM 13.11

In the above problem if we take into account the presence of image force, we will have

$$\begin{aligned} V(x) &= 0 && \text{for} \quad x < 0 \\ &= V_0 - \alpha x - \frac{\beta}{x} && \text{for} \quad x > 0 \end{aligned} \tag{87}$$

Show that the corresponding transmission coefficient is given by

$$T \approx \exp\left[-\frac{4}{3}\left(\frac{2mV_0^3}{\hbar^2\alpha^2}\right)^{1/2}\left(1 - \frac{E}{V_0}\right)^{3/2}\Phi(\Gamma)\right] \tag{88}$$

where

$$\Phi(\Gamma) = \frac{3}{2}\int_{\xi_1}^{\xi_2}\left(1 - \frac{\Gamma}{\xi} - \xi\right)^{1/2} d\xi, \tag{89}$$

$\Gamma = \beta\alpha/(V_0 - E)^2$ and $\xi_{1,2} = \frac{1}{2} \mp (\frac{1}{4} - \Gamma)^{1/2}$ are the roots of the integrand. $\Phi(\Gamma)$ can be expressed in terms of the elliptic integrals (see, e.g., Gradshteyn and Ryzhik, 1965, p. 235)

$$\Phi(\Gamma) = \sqrt{\xi_2}\,[E(\eta) - 2\xi_1 K(\eta)] \tag{90}$$

where $\eta = \left(1 - \frac{\xi_1}{\xi_2}\right)$ and

$$E(\eta) = \int_0^{\pi/2} (1 - \eta \sin^2\theta)^{1/2}\, d\theta$$

and

$$K(\eta) = \int_0^{\pi/2} (1 - \eta \sin^2\theta)^{-1/2}\, d\theta$$

are complete elliptic integrals of first and second kind have been tabulated by Abramowitz and Stegun (1965), p. 608. For $\Gamma = 0.0$, 0.0454, 0.114, 0.160, 0.22 and 0.25 the values of $\Phi(\Gamma)$ are 1.0, 0.765, 0.485, 0.312, 0.094 and 0.0 respectively.

PROBLEM 13.12

(a) In Sec. 4.3 we had considered tunnelling through a rectangular ba
height V_0 and width a (see Fig. 4.2). Show that for $[(2m/\hbar^2)(V_0 - E)\, a^2$
the transmission coefficient is given by

$$T \approx C \exp\left[-2\left(\frac{2m}{\hbar^2}(V_0 - E)\right)^{1/2} a\right]$$

where the factor C is of the order of unity and for certain values
exactly equal to unity.

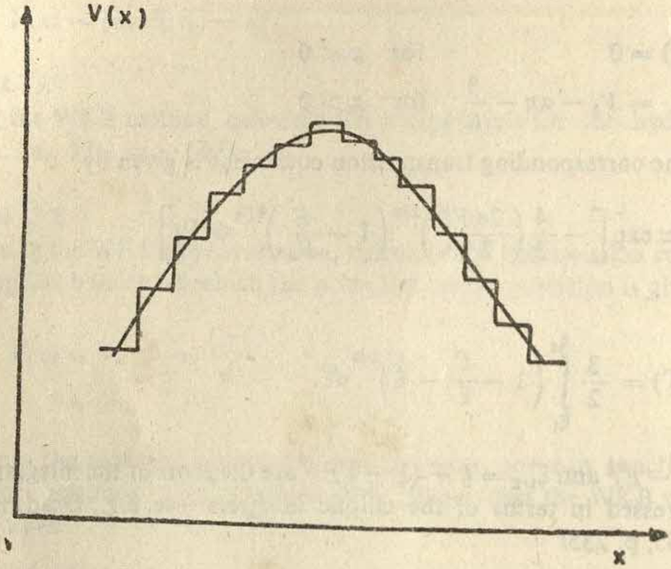

Fig. 13.8 A smooth potential barrier replaced by a large number of steps.

(b) If we now assume $C = 1$ and that a potential of the type shown in Fig. 13.8 is replaced by a series of rectangular steps then by using the above expression for T repeatedly, show that one obtains the WKB result.

Problem 13.13

Equation (8) is known as the WKB solution of Eq. (5). Show that the next approximation gives

$$\psi(x) = \frac{1}{\sqrt{k(x)}} \exp\left(\pm i \int k(x)dx \right) \exp\left[-i\left(\frac{1}{2} \frac{1}{k^2} \frac{dk}{dx} + \frac{1}{4} \int \frac{1}{k^3} \frac{d^2k}{dx^2} dx \right) \right] \tag{91}$$

Problem 13.14

Prove the connection formulae given by Eqs. (18) and (19).

Problem 13.15

In Sec. 13.4 we had used the WKB approximation to calculate the tunnelling probability through a potential barrier. In this problem we will derive a more accurate expression by using the connection formulae in the reverse direction also. In region III, assume a wavefunction of the form

$$\psi_{\text{III}} = \frac{A}{\sqrt{k(x)}} \exp\left[i\left(\int_b^x k(x)\,dx + \frac{\pi}{4} \right) \right] \tag{92}$$

Write ψ_{III} in terms of cosine and sine functions and using the connection formulae given by Eqs. (16)-(19) show that

$$\psi_I \approx \frac{A}{\sqrt{k}}\left[\left(\frac{1}{\theta}+\frac{\theta}{4}\right)\exp\left[i\left(\int_a^x k(x)dx+\frac{\pi}{4}\right)\right]\right.$$

$$\left.+\left(\frac{1}{\theta}-\frac{\theta}{4}\right)\exp\left[-i\left(\int_a^x k(x)+\frac{\pi}{4}\right)\right]\right] \tag{93}$$

where θ is defined through Eq. (46). Thus

$$T=\frac{1}{\left(\frac{1}{\theta}+\frac{\theta}{4}\right)^2} \tag{94}$$

and

$$R=\frac{\left(\frac{1}{\theta}-\frac{\theta}{4}\right)^2}{\left(\frac{1}{\theta}+\frac{\theta}{4}\right)^2} \tag{95}$$

Notice that $R+T=1$.

PROBLEM 13.16

Consider a symmetrical potential well surrounded by a barrier as shown in Fig. 13.9. Calculate the reflection and transmission coefficients for a wave which is incident from the left; the corresponding energy E is denoted by a horizontal

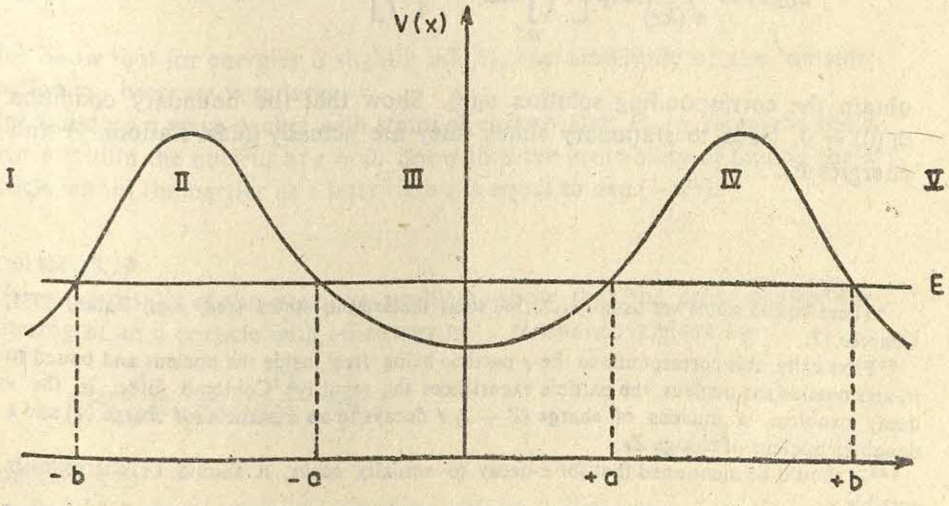

Fig. 13.9 A symmetrical potential well surrounded by a barrier. The points $x = \pm a$ and $x = \pm b$ are turning points.

line in Fig. 13.9. Show that the transmission coefficient is unity when

$$\int_{-a}^{+a} k(x)dx = (n + \tfrac{1}{2})\pi \tag{96}$$

which is the quantization condition for a bound state in the potential well.* (*Hint* : In region V, assume a wavefunction of the form given by Eq. 92, write it in terms of sine and cosine functions and use the connection formulae (16)-(19) in the reverse direction also).

PROBLEM 13.17

This and the following two problems are on the application of the WKB method to α decay. The potential as seen by an α particle is approximately given by** (see Fig. 13.10)

$$\begin{aligned} V(r) &= -V_0 \quad \text{for} \quad r < R \\ &= \frac{z\,Ze^2}{r} \quad \text{for} \quad r > R \end{aligned} \tag{97}$$

where R represents the radius of the nucleus, ze and Ze the charge of the alpha particle and the nucleus respectively. Assuming $l = 0$, calculate the lifetime for α decay***.

PROBLEM 13.18

The potential as seen by an α particle in a nucleus is shown in Fig. 13.10.

(*a*) Starting from a radial function ($\psi = u/r$)

$$u_{\mathrm{III}}(r) = \frac{A}{\sqrt{(kr)}}\exp\left[i\left(\int_a^r k\,dr + \frac{\pi}{4}\right)\right] \tag{98}$$

obtain the corresponding solution $u_{\mathrm{I}}(r)$. Show that the boundary condition $u_{\mathrm{I}}(0) = 0$, leads to stationary states (they are actually quasi-stationary) with energies E_r.

---

*These bound states are usually referred to as metastable states (see, e.g., Bohm, 1951, Chapter 12).

**Physically, this corresponds to the α particle being 'free' inside the nucleus and bound to it, and outside the nucleus, the particle experiences the repulsive Coulomb force. In the α decay problem, a nucleus of charge $(Z + 2)\,e$ decays to an α particle (of charge $2e$) and a daughter nucleus of charge Ze.

***It should be mentioned that for α-decay to actually occur, it should be energetically possible.

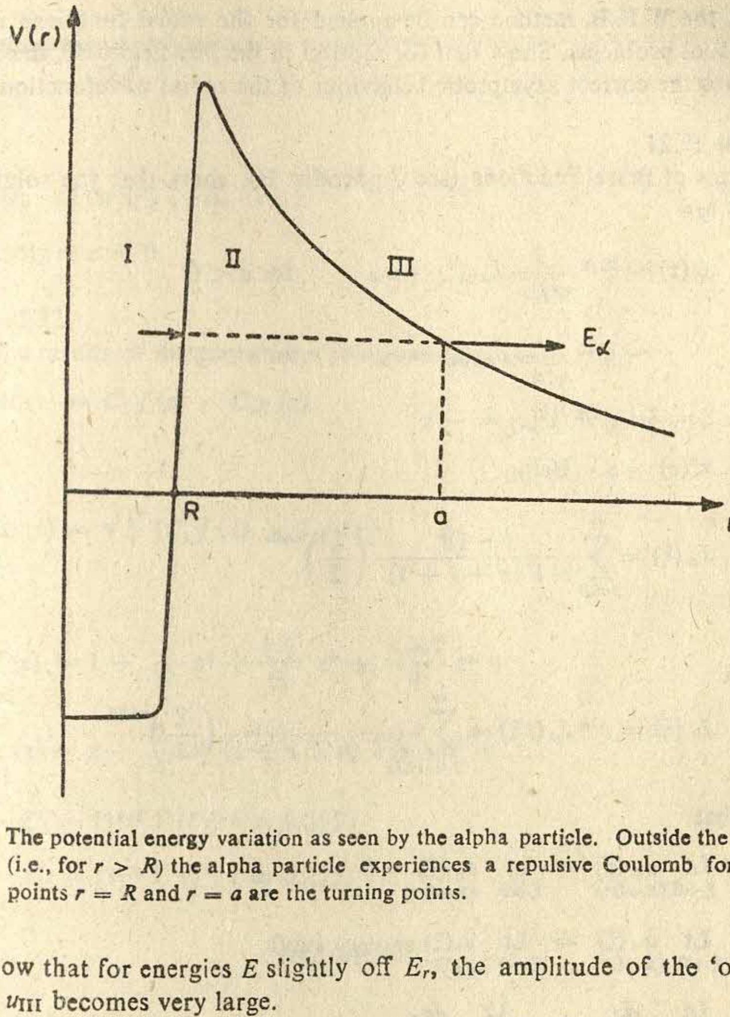

Fig. 13.10 The potential energy variation as seen by the alpha particle. Outside the nucleus (i.e., for $r > R$) the alpha particle experiences a repulsive Coulomb force. The points $r = R$ and $r = a$ are the turning points.

(*b*) Show that for energies E slightly off E_r, the amplitude of the 'outside' function u_{III} becomes very large.

(*c*) Build up a wave packet with states of energy $E \approx E_r$ to represent the α particle within the nucleus at $t = 0$. Show that the probability of finding the α particle within the barrier at a later time t is equal to $\exp(-t/\tau)$.

PROBLEM 13.19

Using the results of the previous problem, show that the cross-section for scattering of an α particle with an energy near resonance is given by

$$\sigma \approx \frac{4\pi}{k^2} \frac{\Gamma^2}{(E - E_r)^2 + \Gamma^2/4} \tag{99}$$

PROBLEM 13.20

In Sec. 13.5, it was mentioned that with the replacement of $l(l + 1)$ b

$(l+\frac{1}{2})^2$, the W.K.B. method can be applied for the radial functions in three dimensional problems. Show that for motion in the free field case, this replacement gives the correct asymptotic behaviour of the radial wavefunction.

PROBLEM 13.21

In terms of Bessel functions (see Appendix H), show that the solutions of Eq. (54) are

$$\psi(z) \sim \xi^{1/2} \frac{1}{\sqrt{k}} J_{\pm\frac{1}{3}}(\xi) = u_\pm \qquad \text{for } z < 0 \tag{100}$$

$$\sim \xi^{1/2} \frac{1}{\sqrt{\kappa}} I_{\pm\frac{1}{3}}(\xi) = v_\pm \qquad \text{for } z > 0 \tag{101}$$

where $\xi = \frac{2}{3}\,|\,z|^{3/2},\ k^2(z) = -z$

and $\kappa^2(z) = z$. Using

$$J_n(\xi) = \sum_{r=0}^{\infty} \frac{(-1)^r}{r!\,\Gamma(n+r+1)} \left(\frac{\xi}{2}\right)^{n+2r} \tag{102}$$

and

$$I_n(\xi) = i^{-n} J_n(i\,\xi) = \sum_{r=0}^{\infty} \frac{1}{r!\,\Gamma(n+r+1)} \left(\frac{\xi}{2}\right)^{n+2r} \tag{103}$$

prove that

$$\underset{\xi\to 0\,(x\to 0^+)}{\text{Lt}}\ u_+(\xi) = \underset{\xi\to 0\ \ (x\to 0^-)}{\text{Lt}}\ v_+(\xi) = 0 \tag{104a}$$

$$\underset{\xi\to 0\ \ (x\to 0^-)}{\text{Lt}}\ u_-(\xi) = \underset{\xi\to 0\,(x\to 0^-)}{\text{Lt}}\ v_-(\xi) = +g_1 \text{ (say)} \tag{104b}$$

$$\underset{\xi\to 0}{\text{Lt}}\ \frac{du_+}{dx} = -\underset{\xi\to 0}{\text{Lt}}\ \frac{dv_+}{dx} = +g_2 \text{ (say)} \tag{105a}$$

and

$$\underset{\xi\to 0}{\text{Lt}}\ \frac{du_-}{dx} = \underset{\xi\to 0}{\text{Lt}}\ \frac{dv_-}{dx} = 0 \tag{105b}$$

Thus u_+ and u_- join smoothly to $-v_+$ and v_- respectively. Hence

$$Ai(z) \equiv \sqrt{\frac{1}{6}}\left[-v_+ + v_-\right] \tag{106a}$$

and

$$Ai(-z) \equiv \sqrt{\frac{1}{6}}\left[u_+ + u_-\right] \tag{106b}$$

join smoothly at $z = 0$. Further

$$Bi(z) \equiv \frac{1}{\sqrt{2}}\,[v_+ + v_-] \tag{107a}$$

and

$$Bi(-z) \equiv \sqrt{\tfrac{1}{2}}\,[-u_+ + u_-] \tag{107b}$$

join smoothly at $z = 0$.

PROBLEM 13.22

Using the results of the previous problem prove that

$$Ai\,(z) = C_1 f\,(z) - C_2 g\,(z) \tag{108}$$

and

$$Bi\,(z) = \sqrt{3}\,[C_1 f\,(z) + C_2 g\,(z)] \tag{109}$$

where

$$f\,(z) = 1 + \frac{1}{3!} z^3 + \frac{1.4}{6!} z^6 + \frac{1.4.7}{9!} z^9 + \dots$$

$$g\,(z) = z + \frac{2}{4!} z^4 + \frac{2.5}{7!} z^7 + \frac{2.5.8}{10!} z^{10} + \dots$$

$$C_1 = [3^{2/3}\,\Gamma\,(\tfrac{2}{3})]^{-1} \simeq 0.3550$$

$$C_2 = [3^{1/3}\,\Gamma\,(\tfrac{1}{3})]^{-1} \simeq 0.2558$$

SOLUTIONS

SOLUTION 13.1

The quantization condition [Eq. (47)] becomes

$$\left(\frac{2m}{\hbar^2}\right)^{1/2} \int_{-a}^{+a} \left[E - \frac{1}{2} m\omega^2 x^2\right]^{1/2} dx = \left(n + \frac{1}{2}\right)\pi \tag{110}$$

where $a = (2E/m\omega^2)^{\frac{1}{2}}$. The integration gives $E = (n + \frac{1}{2})\,\hbar\omega$ which is the same as obtained by using the exact theory [see Eq. (67) of Chapter 3].

SOLUTION 13.3

The quantization condition immediately leads to

$$\left(\frac{2mV_0a^2}{\hbar^2}\right)^{1/2} J\,(\mathcal{E}) = (n + \tfrac{1}{2})\,\pi \tag{111}$$

where

$$J(\mathcal{E}) = \int_{-\alpha(\mathcal{E})}^{+\alpha(\mathcal{E})} (\operatorname{sech}^2 \xi - \mathcal{E})^{1/2} d\xi$$

$$\mathcal{E} = -E/V_0, \ \xi = \frac{x}{a} \text{ and } \alpha = \operatorname{sech}^{-1}\sqrt{\mathcal{E}}$$

Notice that for bound states $0 < \mathcal{E} < 1$. In order to evaluate $J(\mathcal{E})$ we calculate $dJ/d\mathcal{E}$

$$\frac{dJ}{d\mathcal{E}} = -\frac{1}{2}\int_{-\alpha}^{+\alpha} (\operatorname{sech}^2 \xi - \mathcal{E})^{-1/2}\, d\xi \tag{112}$$

where we have used the relation that if

$$J(x) = \int_{g(x)}^{f(x)} F(x, y)\, dy$$

then

$$\frac{dJ}{dx} = \int_{g(x)}^{f(x)} \frac{\partial F(x, y)}{\partial x}\, dy + F(x, f(x))\frac{df}{dx} - F(x, g(x))\frac{dg}{dx}$$

and in our case the second term on the right hand side vanishes because the integrand vanishes at the upper and lower limits*. The integral on the right hand side of Eq. (112) can now be integrated through the substitution $\eta = \sinh \xi$. The resulting equation can now be integrated w.r.t. $\mathcal{E}$ to give

$$J(\mathcal{E}) = \pi\,[1 - \sqrt{\mathcal{E}}]$$

where we have used the fact that $J(1) = 0$. Thus the energy levels are

$$E = -\frac{\hbar^2}{2\,ma^2}\left[\left(\frac{2mV_0a^2}{\hbar^2}\right)^{1/2} - \left(n + \frac{1}{2}\right)\right]^2 \tag{113}$$

SOLUTION 13.5

The solution in region I, i.e., for $x < -b$ (see Fig. 13.7) should be exponentially decaying and hence of the form

---

*Since in all problems using WKB method, the integrand vanishes at the upper and lower limits, this technique of calculating $J(\mathcal{E})$ is quite often used; see also Problem 13.7.

$$\psi_{\text{I}} = \frac{A}{\sqrt{\kappa}} \exp\left[-\int_{x}^{-b} \kappa \, dx\right]$$

which goes over to (in region II)

$$\psi_{\text{II}} = \frac{2A}{\sqrt{k}} \cos\left[\int_{-b}^{x} k \, dx - \frac{\pi}{4}\right] = \frac{2A}{\sqrt{k}} \cos\left[\theta - \int_{x}^{-a} k \, dx - \frac{\pi}{4}\right]$$

where $\theta = \int_{-b}^{-a} k \, dx$. Thus

$$\psi_{\text{II}} = \frac{2A}{\sqrt{k}}\left[\cos\theta \cos\left(\int_{x}^{-a} k \, dx + \frac{\pi}{4}\right) + \sin\theta \sin\left(\int_{x}^{-a} k dx + \frac{\pi}{4}\right)\right]$$

This goes over to

$$\psi_{\text{III}} = \frac{2A}{\sqrt{\kappa}}\left[\cos\theta \, e^{\lambda} \exp\left(-\int_{x}^{a} \kappa \, dx\right) + \frac{\sin\theta}{2} \, e^{-\lambda} \exp\left(\int_{x}^{a} \kappa \, dx\right)\right]$$

in the region $-a < x < a$; here $\lambda = \exp\left(\int_{-a}^{a} \kappa(x) dx\right)$. The condition that the wavefunction should either be symmetric ($\psi'(0) = 0$) or antisymmetric function of x ($\psi(0) = 0$) leads to the required transcendental equation.

SOLUTION 13.6

It is easy to show that

(i) for $0 < \mathcal{E} < \mathcal{E}_0$ one gets

$$\cot\left(\frac{\pi}{2}\mathcal{E}\right) = \pm\frac{1}{2}\exp\left[-\mathcal{E}_0^{1/2}(\mathcal{E}_0 - \mathcal{E})^{1/2} + \mathcal{E}\cosh^{-1}\left(\frac{\mathcal{E}_0}{\mathcal{E}}\right)^{1/2}\right] \tag{114a}$$

and (ii) for $\mathcal{E} > \mathcal{E}_0$ one gets

$$\frac{\pi}{2}\mathcal{E} + \mathcal{E}_0^{1/2}(\mathcal{E} - \mathcal{E}_0)^{1/2} + \mathcal{E}\sin^{-1}\left(\frac{\mathcal{E}_0}{\mathcal{E}}\right)^{1/2} = \left(n + \frac{1}{2}\right)\pi \tag{114b}$$

where

$$\mathcal{E} = \frac{2E}{\hbar\omega} \quad \text{and} \quad \mathcal{E}_0 = m\omega a^2/\hbar$$

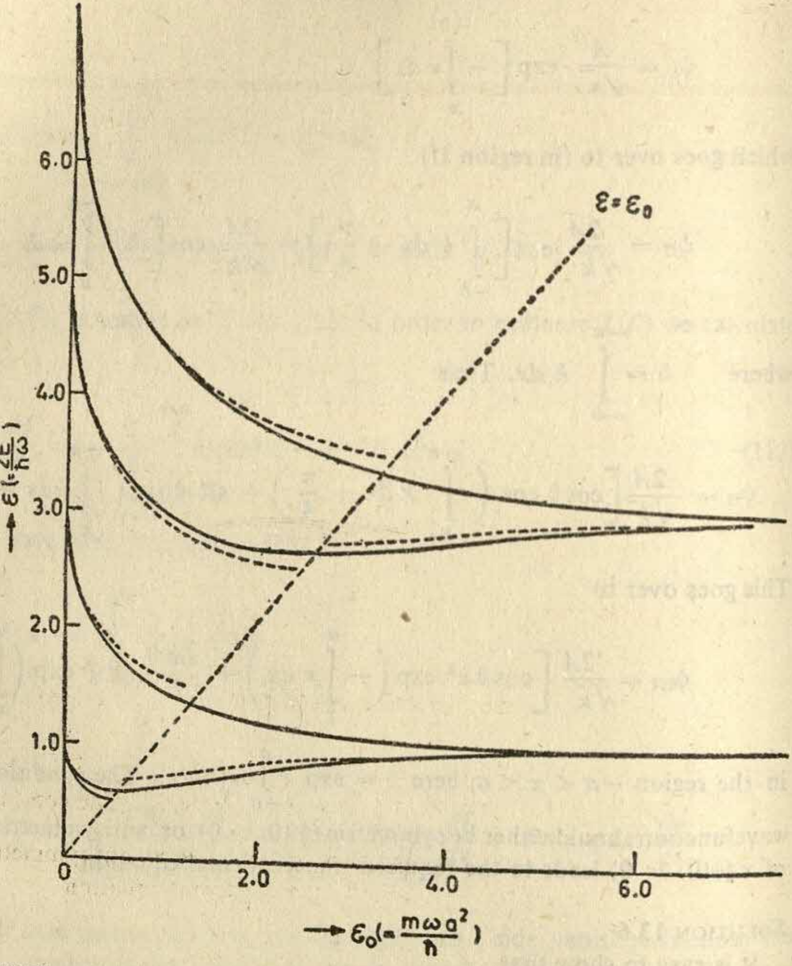

Fig. 13.11 The energy eigen values for the double oscillator as a function of $\mathcal{E}_0$ ($= m\omega a^2/\hbar$) which determines the separation of the two oscillators. The solid and the dashed curves correspond to the exact and WKB calculations respectively. Notice that as $a \to \infty$, $E \to (n + \frac{1}{2})\, \hbar\omega$ and the levels become 2-fold degenerate; thus the system becomes equivalent to two independent harmonic oscillators.

In Fig. 13.11 we have plotted the WKB results and compared them with the exact solutions (see Problem 3.15). Notice that near the line $\mathcal{E} = \mathcal{E}_0$, the WKB results become inaccurate.

SOLUTION 13.7

The quantization condition [Eq. (52)] can be written in the form

$$\sqrt{2}\, J(\mathcal{E}) = (n + \tfrac{1}{2})\, \pi \tag{115}$$

where

$$J(\mathcal{E}) = \int_{\xi_1}^{\xi_2} [-\mathcal{E} - V_{\rm eff}(\xi)]^{1/2} d\xi$$

$$V_{\rm eff}(\xi) = -\frac{Z}{\xi} + \frac{\alpha}{\xi^2}$$

$$\mathcal{E} = -E\Big/\left(\frac{me^4}{\hbar^2}\right), \alpha = \frac{1}{2}\left(l + \frac{1}{2}\right)^2, \quad \xi = \frac{r}{(\hbar^2/me^2)}$$

Using a method similar to that employed in Problem 13.3 one obtains

$$\frac{dJ}{d\mathcal{E}} = -\frac{\pi Z}{4\mathcal{E}^{3/2}} \tag{116}$$

Further the minimum value of $V_{\rm eff}(\xi)$ is $-Z^2/4\alpha$ which occurs at $\xi = 2\alpha/Z$. Thus

$$J\left(\mathcal{E} = -\frac{Z^2}{4\alpha}\right) = 0 \tag{117}$$

because ξ_1 becomes equal to ξ_2. Equation (116) can now be integrated and using Eq. (117) one obtains the following expression from the quantization condition

$$\mathcal{E} = \frac{Z^2}{2(n + l + 1)^2} \tag{118}$$

which is the exact result with $(n + l + 1)$ representing the total quantum number.

SOLUTION 13.8

$$T \approx \exp\left[-2\int_{-x_0}^{x_0}\left[\frac{2m}{\hbar^2}\left(E - V_0\left\{1 - \frac{|x|}{a}\right\}\right)\right]^{1/2} dx\right]$$

where $x = \pm x_0 = \pm(1 - E/V_0)\, a$ are the turning points. Simple integration gives

$$T = \exp\left[-\frac{8}{3}\left(\frac{2mV_0a^2}{\hbar^2}\right)^{1/2}\left(1 - \frac{E}{V_0}\right)^{3/2}\right] \tag{119}$$

SOULTION 13.10

$$\text{(a) } T \approx \exp\left[-2\int_0^{x_1}\left(\frac{2m}{\hbar^2}\right)^{1/2}\left\{V_0 - \alpha x - E_n\right\}^{1/2} dx\right]$$

where $E_x \equiv p_x^2/2m$ and $x_1 = (1/\alpha)(V_0 - E_x)$. Carrying out the integration one gets

$$T \approx \exp\left[-\frac{4}{3\alpha}\left(\frac{2m}{\hbar^2}\right)^{1/2}\left(V_0 - E_x\right)^{3/2}\right] \tag{120}$$

(b) The current density is given by

$$J = (-q_e) \int T \frac{p_x}{m} n(p_x)\, dp_x \tag{121}$$

where $n(p_x)\,dp_x$ represents the number of electrons per unit volume whose p_x lies between p_x and $p_x + dp_x$. Now at low temperatures (i.e., $T \ll E_F/k$), the Fermi function is approximately given by:

$$\begin{aligned} F(E) &= 1 \quad \text{for} \quad E < E_F \\ &= 0 \quad \text{for} \quad E > E_F \end{aligned}$$

(see Problem 5.3). Using the expression for density of states (see Appendix M), we get

$$n(p_x)\, dp_x = \frac{2}{h^3}\, dp_x \iint dp_y\, dp_z$$

$$= \frac{2}{h^3}\, dp_x \int_0^{2\pi} d\theta \int_0^{[2m(E_F - E_x)]^{1/2}} p_1\, dp_1$$

where we have changed into polar co-ordinates and $p_1 = (p_x^2 + p_y^2)^{1/2}$. Thus

$$n(p_x)\, dp_x = \frac{4\pi m}{h^3}(E_F - E_x)\, dp_x \tag{122}$$

Substituting this in Eq. (121), we get

$$J = \frac{4\pi m\,|q|}{h^3} \int_0^{E_F} \exp\left[-\beta\, \phi^{3/2}\left(1 + \frac{\eta}{\phi}\right)^{3/2}\right] \eta\, d\eta$$

where $\eta = E_F - E_x$, $\phi = V_0 - E_F$, $\beta = (4/3\alpha)(2m/\hbar^2)^{1/2}$. Making a binomial expansion of $(1 + \eta/\phi)^{3/2}$, retaining up to first order term and extending the upper limit to ∞, we get

$$J \approx A_0\, \mathcal{E}^2 \exp(-B_0/\mathcal{E}) \tag{123}$$

where we have used $\alpha = |q|\, \mathcal{E}$ and

$$A_0 = \frac{|q|^2}{8\pi h \Phi} = \frac{1.54 \times 10^{-6}}{\Phi}\ \text{amp/m}^2 \tag{124}$$

$$B_0 = \frac{4}{3}\,|q|^{1/2}\left(\frac{2m}{\hbar^2}\right)^{1/2} \Phi^{3/2} = 6.85 \times 10^9\ \Phi^{3/2}\ \text{volts}/m \tag{125}$$

$\Phi = \phi/|q|$ being the work function measured in electron volts. Equation (123) is known as the Fowler-Nordheim field emission formula and agrees with the experimental data. Notice that the field emission (or, sometimes referred to as cold emission) is due to the tunneling phenomenon and hence is a purely quantum mechanical effect.

SOLUTION 13.16

Referring to Fig. 13.9, in region V, (i.e., $x > b$), we have an outgoing wave and hence the wave function would be of the form

$$\psi^{\mathrm{V}} = \frac{A}{\sqrt{k}} \exp\left[i \left(\int_b^x k(x)\, dx + \frac{\pi}{4} \right) \right]$$

$$= \frac{A}{\sqrt{k}} \left[\cos\left(\int_b^x k(x) dx + \frac{\pi}{4} \right) + i \sin\left(\int_b^x k(x)\, dx + \frac{\pi}{4} \right) \right] \tag{126}$$

which would go over to [see Eqs. (18) and (19)]

$$\psi_{\mathrm{IV}} = \frac{A}{\sqrt{\kappa}} \left[\frac{1}{\theta} \exp\left(-\int_a^x \kappa\, dx \right) + \frac{i}{2}\, \theta \exp\left(\int_a^x \kappa\, dx \right) \right] \tag{127}$$

where

$$\theta \equiv \exp\left[-\int_a^b \kappa(x)\, dx \right]$$

Thus

$$\psi_{\mathrm{III}} = \frac{A}{\sqrt{k}} \left[\frac{2}{\theta} \sin\left(\int_x^a k dx + \frac{\pi}{4} \right) + \frac{i\theta}{2} \cos\left(\int_x^a k dx + \frac{\pi}{4} \right) \right]$$

$$= \frac{A}{\sqrt{k}} \left[\left(\frac{2}{\theta} \cos\alpha - \frac{i\theta}{2} \sin\alpha \right) \sin\left(\int_{-a}^x k dx + \frac{\pi}{4} \right) \right.$$

$$\left. - \left(\frac{2}{\theta} \sin\alpha + \frac{i\theta}{2} \cos\alpha \right) \cos\left(\int_{-a}^x k dx + \frac{\pi}{4} \right) \right] \tag{128}$$

where

$$\alpha = \int_{-a}^{+a} k(x) dx - \frac{\pi}{2} \tag{129}$$

We again use the connection formula to obtain

$$\psi_{\text{II}} = \frac{A}{\sqrt{K}}\left[\left(\frac{2}{\theta}\cos\alpha - \frac{i\theta}{2}\sin\alpha\right)\frac{0}{2}\exp\left(\int_{-b}^{x}\kappa(x)\,dx\right)\right.$$
$$\left.-\left(\frac{2}{\theta}\sin\alpha + \frac{i\theta}{2}\cos\alpha\right)\frac{1}{\theta}\exp\left(-\int_{-b}^{x}\kappa(x)\,dx\right)\right] \tag{130}$$

and

$$\psi_{\text{I}} = \frac{A}{\sqrt{k(x)}}\left[\left(\cos\alpha - \frac{i\theta^2}{4}\sin\alpha\right)\cos\left(\int_{x}^{-b} k(x)\,dx + \frac{\pi}{4}\right)\right.$$
$$\left.-\left(\frac{4}{\theta^2}\sin\alpha + i\cos\alpha\right)\sin\left(\int_{x}^{-b} k(x)\,dx + \frac{\pi}{4}\right)\right]$$
$$= \frac{A}{\sqrt{k(x)}}\left(\frac{1}{2}\left\{2\cos\alpha - i\left(\frac{4}{\theta^2} + \frac{\theta^2}{4}\right)\sin\alpha\right\}\right.$$
$$\exp\left\{i\int_{-b}^{x} k(x)\,dx - \frac{i\pi}{4}\right\} + \frac{i}{2}\left(\frac{4}{\theta^2} - \frac{\theta^2}{4}\right)\sin\alpha$$
$$\left.\exp\left\{-i\int_{-b}^{x} k(x)\,dx + \frac{i\pi}{4}\right\}\right] \tag{131}$$

Thus

$$T = \frac{4}{\left[4\cos^2\alpha + \left(\frac{4}{\theta^2} + \frac{\theta^2}{4}\right)^2\sin^2\alpha\right]} \tag{132}$$

and

$$R = \frac{\left(\frac{4}{\theta^2} - \frac{\theta^2}{4}\right)^2\sin^2\alpha}{\left[4\cos^2\alpha + \left(\frac{4}{\theta^2} + \frac{\theta^2}{4}\right)^2\sin^2\alpha\right]} \tag{133}$$

Notice that $R + T = 1$ and further $T = 1$ (and $R = 0$) when

$$\alpha = N\pi \tag{134}$$

or

$$\int_{-a}^{+a} k(x)\,dx = (N + \tfrac{1}{2})\pi \tag{135}$$

This result may be compared to the transmission resonance corresponding to the square well (see Sec. 19.5.2). It may be noted that for a single barrier of the type discussed in Sec. 13.4 the transmission probability is usually extremely small; however, we have just shown that two such barriers with a potential well in between can be completely transparent. This is due to the destructive interference of waves similar to that occurring in a Febry-Perot interferometer.

SOULTION 13.17

$$T \approx \exp(-2J) \tag{136}$$

where

$$J = \left(\frac{2mzZe^2}{\hbar^2} \right)^{1/2} \int_R^a \left(\frac{1}{r} - \frac{1}{a} \right)^{1/2} dr$$

Making the substitution $r = a \cos^2\theta$, we readily get

$$J = \left(\frac{2\, m\, z\, Z\, e^2}{\hbar^2} a \right)^{1/2} \left[\cos^{-1} \left(\frac{R}{a} \right)^{1/2} - \left(\frac{R}{a} - \frac{R^2}{a^2} \right)^{1/2} \right] \tag{137}$$

where a $(= zZe^2/E)$ represents the turning point (see Fig. 13.10). Now, if the speed of α particles inside the nucleus is $\sim v$ then the rate of hitting the barrier $\sim v/R$. Thus the probability per second of escape (which is the inverse of the mean life time) is given by

$$\frac{1}{\tau} \approx \frac{v}{R} e^{-2J} \tag{138}$$

Since* $v \sim 10^9$ cm/sec and $R \sim 10^{-12}$ cm, $v/R \sim 10^{21}$ sec^{-1}. Further, for low energy α particles, $R/a \ll 1$ so that the quantity inside the square brackets in Eq. (137) is $\approx \pi/2$. Thus

$$J \simeq \pi z Z \alpha \left(\frac{mc^2}{E} \right)^{1/2} \tag{139}$$

where $\alpha = e^2/\hbar c \approx 1/137$ is the fine structure constant. Thus one may write

$$\log_{10} \frac{1}{\tau} = C_1 - C_2 \frac{Z}{\sqrt{E}} \tag{140}$$

which can be shown to have a fairly good agreement with experimental data (see, e.g., Hyde *et al.*, 1964). We conclude by noting that the effect of introducing the term $l\,(l + 1)\, \hbar^2/2mr^2$ in $V(r)$ is not very great, because, e.g., for $l \approx 5$, the value of τ changes by a factor not more than 10.

---

*This follows from the uncertainty principle

$$v \sim \frac{h}{mR} \sim \frac{6 \times 10^{-27} \text{ erg-sec}}{(4 \times 1840 \times 9 \times 10^{-28} \text{ g}) \times 10^{-12} \text{ cm}} \sim 10^9 \text{ cm/sec}$$

SOLUTION 13.18

The potential energy of the α particle is of the form shown in Fig. 13.10. We look for solution in region III which represents an outgoing wave. Thus

$$u_{\text{III}}(r) = \frac{A}{\sqrt{k(r)}} \exp\left[i \int_a^r k(r) dr + i \frac{\pi}{4} \right] \tag{141}$$

where the constant $e^{i\pi/4}$ has been introduced for convenience. Expressing in terms of sine and cosine functions and using Eqs. (18) and (19), $u_{\text{III}}(r)$ goes over to (in region II)

$$u_{\text{II}}(r) = \frac{A}{\sqrt{\kappa}} \left\{ \frac{1}{T} \exp\left(- \int_R^r \kappa dr \right) + \frac{i}{2} T \exp\left(+ \int_R^r \kappa(r)\, dr \right) \right\} \tag{142}$$

where

$$T = \exp\left[- \int_R^a \kappa(r) dr \right] \tag{143}$$

$u_{\text{II}}(r)$ would go over to [see Eqs. (16) and (17)]

$$u_{\text{I}}(r) = \frac{A}{\sqrt{k}} \left\{ \frac{2}{T} \sin\left(\int_r^R k dr + \frac{\pi}{4} \right) + \frac{i}{2} T \cos\left(\int_r^R k dr + \frac{\pi}{4} \right) \right\}$$

$$\approx \frac{N}{\sqrt{k}} \sin\left(\int_r^R k(r) dr + \frac{\pi}{4} \right) \quad (\text{for } T \ll 1) \tag{144}$$

where $N = 2A/T$. Now, the boundary condition $u_{\text{I}}(0) = 0$ (otherwise $\psi = u(r)/r$ will go to ∞) gives

$$\sin\left[\int_0^R k(r)\, dr + \frac{\pi}{4} \right] = 0$$

or

$$\int_0^R k(r)\, dr = \left(n - \frac{1}{4} \right) \pi; \; n = 1, 2, \ldots \tag{145}$$

which would be satisfied for certain values of E which we denote by E_r. When the energy of the particle is slightly different from E_r, we may write, for $u_{\text{I}}(r)$

$$u_{\mathrm{I}}^{E} = \frac{N_E}{\sqrt{k}} \sin\left(\int_r^R k dr + \frac{\pi}{4} - \theta\right) \tag{146}$$

Now, we may write

$$k \simeq k_r + \left(\frac{\partial k}{\partial E}\right)_r (E - E_r)$$

$$\simeq k_r + \frac{1}{\hbar v_r} (E - E_r)$$

where v_r (= $\hbar k r/m$) is the velocity. Thus $u_{\mathrm{I}}^{E}(0)$ gives

$$\sin\left(\int_0^R k_r \, dr + \frac{\pi}{4} + (E - E_r) \frac{1}{\hbar} \int_0^R \frac{dr}{v_r} - \theta\right) = 0$$

which will be satisfied if

$$\theta = \frac{E - E_r}{\hbar} \tau_0 \tag{147}$$

where

$$\tau_0 = \int_0^R \frac{dr}{v_r} \tag{148}$$

Let us now obtain, from the connection formulae, the wavefunction u_{II}^{E} and u_{III}^{E} corresponding to Eq. (146). Writing

$$u_{\mathrm{I}}^{E} = \frac{N_E}{\sqrt{k}} \left[\cos\theta \sin\left(\int_r^R k dr + \frac{\pi}{4}\right) - \sin\theta \cos\left(\int_r^R k dr + \frac{\pi}{4}\right)\right] \tag{149}$$

we get

$$u_{\mathrm{II}}^{E} = \frac{N_E}{\sqrt{\kappa}} \left[\frac{T}{2} \cos\theta \exp\left(\int_r^a \kappa(r) \, dr\right) - \frac{\sin\theta}{T} \exp\left(-\int_r^a \kappa(r) \, dr\right)\right] \tag{150}$$

and

$$u_{\mathrm{III}}^{E} = \frac{N_E}{\sqrt{\kappa}} \left[\frac{T}{2} \cos\theta \cos\left(\int_a^r k dr + \frac{\pi}{4}\right) - \frac{2\sin\theta}{T} \sin\left(\int_a^r k dr + \frac{\pi}{4}\right)\right] \tag{151}$$

From Eq. (151) it can be seen that unless $\sin\theta \simeq 0$, the second term can be very large so that the probability of finding the particle outside is large except at certain energies $E = E_r$ ($\theta = 0$). Rewriting this equation in the form

$$u_{\mathrm{III}}^{E} = \frac{N_E}{\sqrt{k}} A \cos\left[\int_a^r k(r) \, dr + \frac{\pi}{4} + \delta\right] \tag{152}$$

we get

$$A = \left(\frac{\cos^2\theta}{4}T^2 + \frac{4}{T^2}\sin^2\theta\right)^{1/2} \text{ and} \tag{153}$$

$$\tan\delta = \frac{4}{T^2}\tan\theta \tag{154}$$

Notice that for small values of T, as θ goes from negative to positive values (i.e., as the energy E passes through resonance) $\tan\delta$ changes rapidly from a large negative value to a large positive value, so that δ changes by π. We may write, for small values of θ

$$A^2 \approx \frac{T^2}{4} + 4\frac{\theta^2}{T^2} \tag{155}$$

The current of α particles in region III is

$$v\,4\pi\left|\overline{u^E_{\rm III}}\right|^2 = v\,|N_E|^2\;\frac{4\pi A^2}{k}\cdot\frac{1}{2} = |N_E|^2\,\frac{2\pi\hbar}{m}A^2 \tag{156}$$

Thus for a unit current of α particles

$$A^2 = \frac{m}{2\pi\hbar\,|N_E|^2}$$

At resonance $\theta = 0$ so that

$$|N_{E_r}|^2 = \frac{m}{2\pi\hbar\,(A^2)_{\theta=0}}$$

Thus

$$\frac{N_E}{N_{E_r}} = \left[\frac{(A)^2_{\theta=0}}{A^2}\right]^{1/2} \simeq \left[1 + \frac{16\theta^2}{T^4}\right]^{-1/2} \tag{157}$$

Let us now build a wave packet to represent the α particle within $r = R$ at $t = 0$.

$$u(r, 0) = \int u^E(r)\,\phi(E - E_r)\,dE$$

$$= \int_{-\infty}^{+\infty} u^{\mathcal{E}}(r)\,\phi(\mathcal{E})\,d\mathcal{E} \tag{158}$$

where $\mathcal{E} = E - E_r$ and $\phi(\mathcal{E})$ will be large only near the region $E = E_r$. We have

$$\phi(\mathcal{E}) = \int_0^{r_1} u^{\mathcal{E}*}(r)\,u(r, 0)\,dr \tag{159}$$

where we have used the relation

$$\int u^{\mathcal{E}'^*}(r)\, u^{\mathcal{E}}(r)\, dr = \delta(\mathcal{E} - \mathcal{E}') \tag{160}$$

The time development of the wave packet is given by

$$u(r, t) = \int_{-\infty}^{+\infty} u^{\mathcal{E}}(r)\, e^{-iEt/\hbar}\, \phi(E - E_r)\, dE \tag{161}$$

The probability $W(t)$ that the α particle is still in the original state is given by

$$W(t) = \left| \int_0^{\infty} u^*(r, 0)\, u(r, t) dr \right|^2 = \left| \int_{-\infty}^{+\infty} |\phi(\mathcal{E})|^2\, e^{-i\mathcal{E}/\hbar}\, d\mathcal{E} \right|^2 \tag{162}$$

where we have used Eq. (160). $\phi(\mathcal{E})$ may be evaluated from Eq. (159). Now, the initial wavefunction $u\,(r, 0)$ is very nearly a stationary state ($\mathcal{E} = 0$); on the other hand, $u^{\mathcal{E}}\,(r)$ differs slightly from the stationary state; therefore we may write

$$\phi(\mathcal{E}) \approx \frac{N_E}{N_{E_r}} = \left[1 + \frac{16\,\mathcal{E}^2 \tau_0^2}{\hbar^2 T^4}\right]^{-1/2} \tag{163}$$

Thus

$$W(t) \propto \left| \int_{-\infty}^{+\infty} \frac{e^{-i\mathcal{E}t/\hbar}}{\left[1 + \frac{16\,\mathcal{E}^2 \tau_0^2}{\hbar^2 T^4}\right]}\, d\mathcal{E} \right|^2 \tag{164}$$

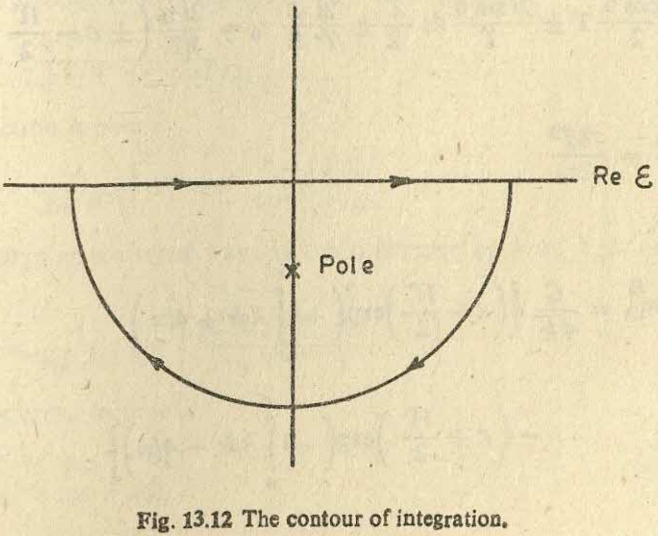

Fig. 13.12 The contour of integration.

This integral may be evaluated (for $t > 0$) over the contour indicated in the complex $\mathcal{E}$ plane (using Jordan's lemma). There is a simple pole (see Fig. 13.12) within the contour at

$$\mathcal{E} = -\frac{i\hbar T^2}{4\tau_0}$$

Evaluating the integral we obtain

$$W(t) \propto | e^{-t/2\tau} |^2 = e^{-t/\tau} \tag{165}$$

where

$$\frac{1}{\tau} = \frac{T^2}{2\tau_0} \tag{166}$$

This result may be compared with Eq. (138).

Solution 13.19

Let us rewrite Eq. (151) in terms of ingoing and outgoing spherical waves

$$u_{\text{III}}^{\mathcal{E}} = \frac{N_E}{\sqrt{k}} \left\{ \left(\frac{\cos\theta}{2} T + \frac{2i\sin\theta}{T} \right) \exp i \left(\int_a^r k dr + \pi/4 \right) \right.$$

$$\left. + \left(\frac{\cos\theta}{2} T - \frac{2i\sin\theta}{T} \right) \exp -i \left(\int_a^r k dr + \pi/4 \right) \right\} \tag{167}$$

Let us examine this in the neighbourhood of resonance, i.e., for small values of $\theta \left(= \frac{\mathcal{E}}{\hbar} \tau_0 \right)$. Thus

$$\frac{\cos\theta}{2} T \pm \frac{2i\sin\theta}{T} \approx \frac{T}{2} \pm \frac{2i}{T} \frac{\mathcal{E}}{\hbar} \tau_0 = \frac{2i\tau_0}{\hbar T} \left(\pm \mathcal{E} - \frac{i\Gamma}{2} \right) \tag{168}$$

where

$$\Gamma = \frac{\hbar T^2}{2\tau_0}$$

Therefore,

$$u_{\text{III}}^{E} = \frac{C}{\sqrt{k}} \left\{ \left(\mathcal{E} - \frac{i\Gamma}{2} \right) \exp\left(+i \int_a^r k dr + 4/\pi \right) \right.$$

$$\left. - \left(\mathcal{E} + \frac{i\Gamma}{2} \right) \exp\left(-i \int_a^r k dr + 4/\pi \right) \right\} \tag{169}$$

We may write the exponents as

$$\int_a^r k dr = \int_a^b k dr + \int_b^r k dr$$

Assuming that for $r > b$ the potential tends to zero, k remains constant and this gives

$$u_{\mathrm{III}}^{E} \xrightarrow[\text{large } r]{} \frac{C}{\sqrt{k}} \left\{ \left(\mathcal{E} - \frac{i\Gamma}{2} \right) \exp i\,(kr + \delta) - \left(\mathcal{E} + \frac{i\Gamma}{2} \right) \exp - i\,(kr + \delta) \right\} \tag{170}$$

consider now a plane wave of unit flux, which undergoes no scattering.

$$\psi = \frac{1}{v^{1/2}} e^{ipz/\hbar} \tag{171}$$

The $l = 0$ part of this wave can be written as (see Appendix N and Eq. 11 of Appendix H):

$$\psi = \frac{1}{2iv^{1/2}} \frac{e^{ikr} - e^{-ikr}}{kr}, \tag{172}$$

or

$$u = \frac{1}{2ik\, v^{1/2}} \left[e^{ikr} - e^{-ikr} \right] \tag{173}$$

Thus unit flux corresponds to an ingoing spherical wave

$$-\frac{1}{2ik\, v^{1/2}} e^{-ikr} \tag{174}$$

We can make this agree with Eq. (170) by requiring

$$C = \frac{k^{1/2}}{2ik\, v^{1/2}} \frac{e^{i\delta}}{(\mathcal{E} + i\Gamma/2)} \tag{175}$$

The wavefunction is now

$$u_{\mathrm{III}} \to \frac{1}{2ik\, v^{1/2}} \left[e^{ikr}\, e^{2i\delta}\, \frac{\mathcal{E} - i\,\Gamma/2}{\mathcal{E} + i\,\Gamma/2} - e^{-ikr} \right] \tag{176}$$

so that the outgoing scattered wave is the difference between Eqs. (176) and (173). Thus

$$u_{\mathrm{SC}} = \frac{1}{2ik\, v^{1/2}}\, e^{ikr} \left\{ \frac{(\mathcal{E} - i\Gamma/2)\, e^{2i\delta}}{(\mathcal{E} + i\Gamma/2)} - 1 \right\}. \tag{177}$$

The scattering cross-section is

$$\begin{aligned} d\sigma &= v\, |\, \psi_{\mathrm{SC}}\, |^2\, r^2 d\Omega \\ &= v\, |\, u_{\mathrm{SC}}\, |^2\, d\Omega \end{aligned}$$

The total cross-section is given by

$$\sigma = \frac{\pi}{k^2}\left|\frac{\mathcal{E} - i\Gamma/2}{\mathcal{E} + i\Gamma/2}\, e^{2i\delta} - 1\right|^2$$

$$= \frac{4\pi}{k^2}\,\frac{(\mathcal{E}\sin\delta - \Gamma/2\cos\delta)^2}{(\mathcal{E}^2 + \Gamma^2/4)} \tag{178}$$

for energies far away from resonance $\mathcal{E} \gg \Gamma$ and

$$\sigma = \frac{4\pi}{k^2}\sin^2\delta \tag{179}$$

while for small δ and small $\mathcal{E}$

$$\sigma = \frac{\pi}{k^2}\,\frac{\Gamma^2}{\mathcal{E}^2 + \Gamma^2/4} \tag{180}$$

CHAPTER FOURTEEN

Hydrogen and Hydrogen Like Atoms

14.1 Energy Levels of Hydrogen: Relativistic Effects

We have seen (in Sec. 5.3) that the non-relativistic theory of the hydrogen atom gives for the energy

$$E_n = -E_R \left(\frac{1}{n^2}\right) \approx -\frac{13.6}{n^2} \text{ eV}$$

so that the energies are independent of the orbital angular momenta l and the magnetic quantum number m. As already mentioned (see Sec 5.3), the l degeneracy is peculiar to the Coulomb potential. Indeed, in the relativistic theory of Dirac, this degeneracy is lifted. An approximate treatment of relativistic effects already shows how this happens (see Problem 11.12).*

The observed spectra of hydrogen show that further features are to be incorporated. The most important of these is the spin orbit correction to the Hamiltonian

$$H_{so} = \xi(r)\, \mathbf{L} \cdot \mathbf{s}$$

With this addition, $\mathbf{L}$ and $\mathbf{s}$ no longer commute with the Hamiltonian. But $\mathbf{J} = \mathbf{L} + \mathbf{s}$ does commute so that the *good* quantum numbers are (see Problem 11.12).

$$l, s, j \text{ and } m = m_l + m_s$$

Here m is the eigenvalue of J_z. For a free atom spherical symmetry still ensures m degeneracy so that the energies depend only on l, s and j.

The splitting of a particular level due to the spin orbit interaction is called the *fine structure* and is worked out in Problem 11.12. Referring to Fig. 11.4, it can be seen that the magnitudes of fine structure splitting and relativity effect are of comparable order and some 10^5 times smaller than the spacing of $n = 1$ and $n = 2$ levels.

14.2 Fine Structure of Hydrogen in Dirac Theory

Dirac's relativistic theory predicts (see Sec. 23.10; see also Problem 11.12) for the hydrogen atom energies

$$E_{n,j} = mc^2 \left[1 - \frac{Z^2\alpha^2}{2n^2} - \frac{Z^4\alpha^4}{2n^4}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) - \cdots\right]$$

Here $\alpha = e^2/\hbar c$, the fine structure constant and the energy $E_{n,j}$ includes the rest energy of the electron.

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*This can be understood qualitatively from the Sommerfeld model of elliptic orbits. For these, the velocity of the electron is not constant and the mass changes differently for different orbits with the same n.

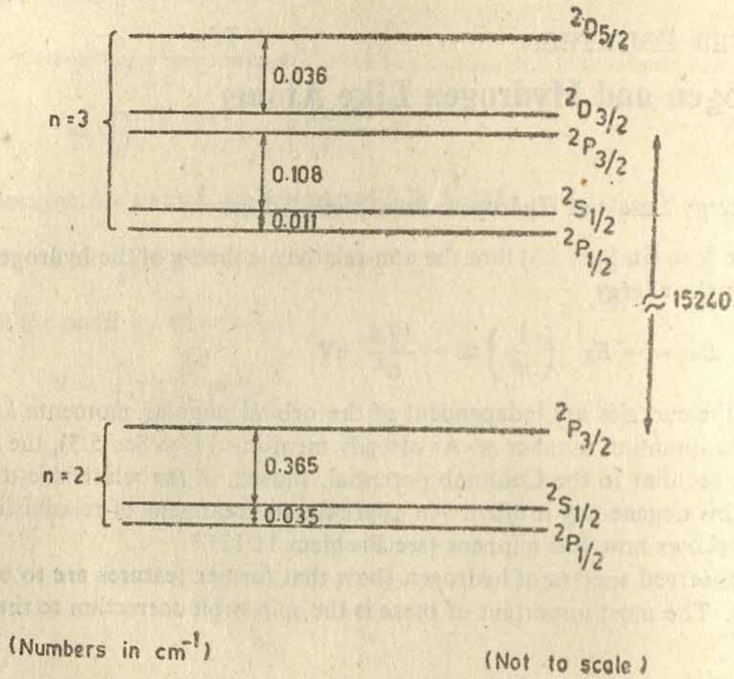

Fig. 14.1. Level structure of the hydrogen atom.

The point to note in this formula is that the energy does not depend explicitly on l so that levels with a particular n and j value will be doubly degenerate with $l = j \pm \frac{1}{2}$ for the two levels (except for $l = 0$). The experimentally observed level structure is shown in Fig. 14.1 for $n = 2$ and $n = 3$. The level splittings are shown in cm^{-1} along with their spectroscopic levels. (For example $^2D_{3/2}$ means $2s + 1 = 2$, i.e., $s = \frac{1}{2}$; $l = 2$ and $j = 3/2$).

The discovery that $2\,^2S_{1/2}$ level lies about 1058 Mc/s* above the $2\,^2P_{1/2}$ level was made in a crucial experiment by Lamb and Retherford in 1947 and it led to important theoretical developments in quantum electrodynamics.

14.3. Alkali Atoms

Next to hydrogen, the simplest spectra are those of alkali atoms, viz. Li, Na, K etc., which have a single s electron outside closed shells. An oversimplified picture for these atoms would be to think of the single electron moving in a Coulomb field in a hydrogen like orbit with $n > 1$. For example, sodium ($1s^2 2s^2 2p^6 3s$) may be thought of as an atom with $3s$ electron moving in the central field due to a single charge, the ten electrons in the closed shells shielding the nuclear charge. The ionization potential of sodium, in this picture, would be

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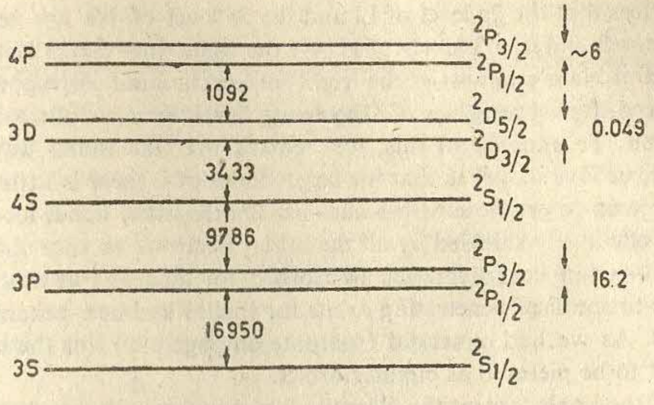
*For such small splittings, it is conventional to quote the frequency ν rather than the energy $h\nu$, 1 Mc/s $\approx 4.14 \times 10^{-9}$ eV.



(Numbers in cm^{-1}) (Not to scale)

Fig. 14.2. Energy levels of Na for the $n=3$ and $n=4$ states of the valence electron.

$1/n^2\,(13.6) \approx 1.5$ eV which is much smaller than the observed value of 5.1 eV. The reason for this large discrepancy is that the 3*s* electron wavefunction yields a finite probability for being close to the nucleus when the potential it sees will be due to an incompletely shielded nucleus. Thus the effective potential experienced by the 3*s* electron is not really $-e/r$ as in the case of hydrogen.

The result is that the levels of alkali atoms, while showing qualitative features of hydrogen, exhibit certain important differences. Fig. 14.2 shows the energy levels of Na for the $n = 3$ and $n = 4$ states of the valence electron.

Note that the 3*S* and 3*P* levels are no longer degenerate. Moreover, each of the levels, 3*P*, 3*D* and 4*P* splits into a pair with $j = l + \frac{1}{2}$ and $l - \frac{1}{2}$. The level spacings are indicated.

A comparison of the energy levels of hydrogen, lithium and sodium is worth a study to bring out the broad features of hydrogen like atoms. Figure 14.3 shows some levels (only the *n*, *l* values are indicated).

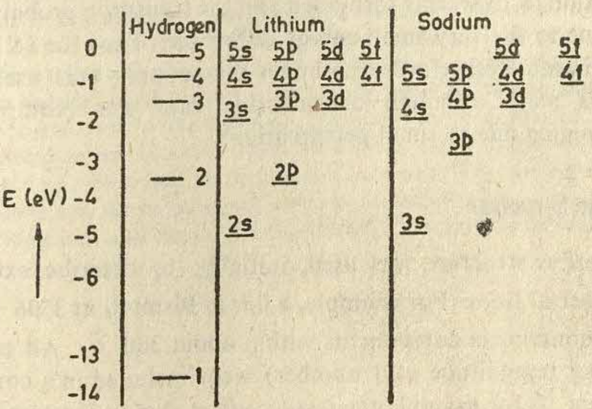


Fig. 14.3. Broad features of the energy levels of hydrogen, lithium and sodium.

One notices that the 2*s* level of Li and the 3*s* level of Na are very different from the $n = 2$ and $n = 3$ levels of H. At the same time the 2*p* level of Li and the 3*d* level of Na are almost at the 'right' places, i.e., the corresponding values of H. Indeed, for large values of l the energy levels seem to follow closely those of hydrogen. To understand this, we remark that the radial wavefunctions, for small r, behave like r^l so that for large values of l, there is little probability for the electron to get close to the nucleus. On the other hand, for large r, the nucleus is effectively shielded by all the other electrons so that the outermost electron moves in near hydrogen like orbits for large l. For this reason, it is customary to speak of penetrating orbits for small l and non-penetrating orbits for large l. As we had remarked (footnote on page 136) it is the large l orbits that ought to be pictured as circular orbits.

Each of the levels (except the S levels) is a doublet with a splitting proportional to $\xi(r)\,\mathbf{L}\cdot\mathbf{s}$ due to the spin orbit interaction. Although the expectation value of $\langle \mathbf{L}\cdot\mathbf{s}\rangle$ increases with l, the value $\langle \xi(r)\rangle$ decreases rapidly with l so that the doublet splitting becomes quite small for large l.

14.4. Selection Rules

The experimental source of information for deducing the level structure discussed, is the observed spectra arising from transitions from one level to another. These transitions are dictated by certain selection rules, the most important for atomic spectra being the ones for electric dipole transitions. These are

$$\Delta l = \pm 1, \qquad \Delta j = 0, \pm 1$$

for the changes in these quantum numbers from the initial to the final atomic state. (The derivation of these rules is given in Chapter 21). A classic example in Na are the '*D*' lines easily observed in optical spectroscopy, the transitions being $3\,{}^2P_{3/2}$ and $3\,{}^2P_{1/2}$ to $3\,{}^2S_{1/2}$.

A most important consequence of these rules for hydrogen arises for the state $2\,{}^2S_{1/2}$. Transition to $1S$ state is forbidden and the transition probability to $2\,{}^2P_{1/2}$ is negligible due to the very small energy difference. Thus the $2S$ state is metastable; in the Lamb-Retherford experiment this property was used to separate atoms in this state although considerable care was required to prevent $2S_{1/2}-2P_{1/2}$ mixing due to small perturbations.

14.5 Hyperfine Structure

The term hyperfine structure was used, initially, to describe extremely small splitting of spectral lines. For example, a line in Bismuth at 3596 A wavelength was found to contain six components within about 300 Å. All effects causing such a splitting (magnitude and number) were included in a consideration of hyperfine effects, as for example the *isotope effect*, due to the sample containing more than one isotope.

The term is *now* used to describe interaction between a particular nucleus and the surrounding electrons. The interaction is then between the electric and magnetic moments of the nucleus and the electric and magnetic fields at the site of the nucleus due to the electrons*.

In this chapter we shall describe the hyperfine splitting of hydrogen—primarily, the ground state. This splitting is due to the interaction of the magnetic moments of the proton and the electron associated with their spins. An estimate may be made from semiclassical considerations. The energy of a pair of parallel magnets separated by a distance r is $\sim \mu_1 \mu_2/r^3$, where μ_1 and μ_2 are magnetic moments. Using this to estimate the energy we have

$$\Delta E_{hf} \sim \left(2.8 \frac{e\hbar}{2Mc}\right)\left(\frac{e\hbar}{2mc}\right)\left\langle\frac{1}{r^3}\right\rangle$$

where the first factor is the proton and the second, the electron magnetic moments. Taking the average $\langle 1/r^3 \rangle \sim 1/a_0^3$ (see Appendix J) where a_0 is the Bohr radius, one obtains

$$\Delta E_{hf} \sim 150 \text{ MHz}$$

A more careful quantum mechanical calculation gives (see also Problem 18.6)

$$\Delta E_{hf} = \mp \mu_e \mu_p [4\pi \psi^2(0)]$$

in energy units, the negative and positive signs corresponding to parallel and antiparallel spin alignment. Here $\psi(0)$ is the $1S$ wavefunction at the origin. This gives

$$\Delta E_{hf} \sim \mp 600 \text{ MHz}$$

The experimentally observed splitting of 1420 MHz** is somewhat larger than this and has been well accounted for in a more careful calculation based on Dirac theory.

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*The idea that the energy of the atom is the sum of a nuclear energy and a portion 'belonging' to the electrons is a fiction of our making, but a convenient fiction at that because the scale of energies of the two is so different. It has become possible to study the hyperfine interaltion both from the nuclear and atomic spectral studies—the enormous accuracy of energy measurement in such methods as Mossbauer spectroscopy has made this possible. Evidently, a study of hyperfine interactions is then a tool to explore nuclear properties or the field due to the surrounding electrons depending on which we know better to begin with. Indeed the growth of the subject may be judged by the fact that an annual international conference on hyperfine interactions is now the source of an enormous amount of data.

**Actually, this value has been determined experimentally to a precision of about 2 parts in 10^{11}.

CHAPTER FIFTEEN

The Helium Atom and the Exclusion Principle

15.1 Introduction

Schrödinger's equation, as we have seen in Chapter 3, gives the same energies for the hydrogen atom as the Bohr model. It is only when we consider many electron systems that new effects are manifested, the most important being those due to the Pauli exclusion principle which is fundamental to an understanding of the building up of the periodic table. In this chapter, we shall first consider the ground state of a two electron system, namely the helium atom and then go on to examine a few excited states in order to understand the basic principles of the study of atomic structure. Many electron atoms will be discussed in the next chapter.

15.2 The Independent Particle Approximation

The potential energy of the helium-like atom contains an extra term, apart from the electron nucleus interaction: namely, the repulsive energy of the two electrons. The Hamiltonian is

$$\begin{aligned} H &= \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \\ &= -\frac{\hbar^2}{2m}\left[\nabla_1^2 + \nabla_2^2\right] - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \qquad (1) \end{aligned}$$

Here, $\mathbf{r}_1$ and $\mathbf{r}_2$ represent the co-ordinates of the two electrons with respect to the nucleus (which is assumed to be stationary) and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the two electrons (see Fig. 15.1) for the helium atom, $Z = 2$. Now the term e^2/r_{12} is of the same order of magnitude as the other two terms in the potential energy; nevertheless, we shall begin by neglecting it. (We shall see, later, how to incorporate this term). The resulting approximation may be called the *independent particle model*. In this approximation, the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}\right) u(\mathbf{r}_1, \mathbf{r}_2) = Eu(\mathbf{r}_1, \mathbf{r}_2) \qquad (2)$$

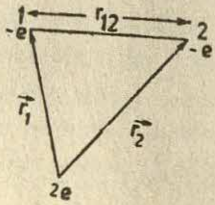

Fig. 15.1 The helium atom consists of a nucleus of charge 2*e* and two electrons.

may be separated by writing

$$u(\mathbf{r}_1, \mathbf{r}_2) = u_a(\mathbf{r}_1)\, u_b\, (\mathbf{r}_2) \tag{3}$$

giving identical equations for u_a and u_b

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{r_1}\right) u_a(\mathbf{r}_1) = E_a\, u_a\, (\mathbf{r}_1) \tag{4}$$

$$\left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_2}\right) u_b(\mathbf{r}_2) = E_b\, u_b\, (\mathbf{r}_2) \tag{5}$$

with $\quad E = E_a + E_b \qquad (6)$

Equations (4) and (5) tell us that the two electrons 1 and 2 move independently of each other and the total energy of the system is simply the sum of the energies of the non-interacting electrons.

Since Eqs. (4) and (5) are the same as for a hydrogen like atom, the solutions are immediately written down (see Secs. 5.2 and 5.3)

$$u_a\, (\mathbf{r}_1) = R_{n_1 l_1}\, (r_1)\; Y_{l_1 m_1}\, (\theta_1, \varphi_1) \tag{7}$$

and a similar one for u_b $(\mathbf{r}_2)$. A particular eigenstate is characterized by specifying a and b, i.e., by specifying the two sets of quantum numbers n_1, l_1, m_1 and n_2, l_2, m_2.

Similarly, the energy eigenvalues can easily be written down. Both E_a and E_b would be of the form*

$$E_n = -\frac{Z^2}{n^2}\frac{me^4}{2\hbar^2} = -\frac{Z^2}{n^2}E_H \tag{8}$$

where

$$E_H = \frac{me^4}{2\hbar^2} = 13.605 \text{ eV} \tag{9}$$

represents the ionization energy of the hydrogen atom. In this approximation, then, the ground state is the one with both electrons in the 1s state (designated as the 1s^2 configuration), the total energy being (for $Z = 2$)

$$-4\, E_H - 4\, E_H = -108.8 \text{ eV} \tag{10}$$

This is to be compared with the observed value of -79.0 eV.

15.3 Electron Interaction Energy

One way to estimate this is to regard e^2/r_{12} as a perturbation. The first order correction to the ground state energy is, then

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \iint u_{100}^*(\mathbf{r}_1)\, u_{100}^*(\mathbf{r}_2)\; \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\; u_{100}\, (\mathbf{r}_1)\, u_{100}\, (\mathbf{r}_2)\, d\tau_1\, d\tau_2 \tag{11}$$

---

*The Hamiltonian given by Eq. (1) assumes infinite mass of the nucleus. The effect of the finite mass of the nucleus can be approximately taken into account by replacing the electron mass m by the reduced mass μ $(= m\, M/(m + M))$ where M is the mass of the nucleus—see Problem 15.6 (cf. Sec. 5.2).

which has been evaluated in Problem 15.1, the result is

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{5}{4} Z E_H \approx 34.02 \text{ eV} \tag{12}$$

Where we have assumed $Z = 2$. Thus the total energy is -74.8 eV, only 4.2 eV above the experimental value. Such a large 'correction' makes the perturbation approach suspect and we turn to other methods.

15.4 Variation Method

The effect of the repulsive term, e^2/r_{12}, is to reduce the nuclear attraction on each electron. One way to accommodate this is to assume hydrogen like wavefunctions corresponding to an effective nuclear charge Z', which will be assumed to be a variable parameter. Thus, we assume the (normalized) wavefunction as [cf. Eq. (60) of Chapter 5]

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \left(\frac{Z'^3}{\pi a_0^3} \right) e^{-Z' r_1/a_0} e^{-Z' r_2/a_0} \tag{13}$$

The Hamiltonian, however, remains as in Eq. (1) with Z as a *fixed* number; for He, $Z = 2$. We have to minimize the integral (see Secs. 12.2 and 12.4).

$$E(Z') = \iint \phi^* \left[-\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - Ze^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{r_{12}} \right] \phi(\mathbf{r}_1, \mathbf{r}_2)\, d\tau_1\, d\tau_2 \tag{14}$$

which has been evaluated in Problem 15.2. The result is

$$E(Z') = \left[-2Z'^2 + 4Z'(Z' - Z) + \frac{5}{4} Z' \right] E_H \tag{15}$$

The minimum of $E(Z')$ occurs when

$$Z' = Z_{\text{eff}} = Z - \frac{5}{16} \approx 1.69 \tag{16}$$

so that

$$\begin{aligned} E &= -2 Z_{\text{eff}}^2 E_H \\ &\approx -76.2 \text{ eV} \end{aligned} \tag{17}$$

Other trial functions (having more complicated forms) have also been used, some yielding values within 0.01% of the observed one—see Table 12.1.

15.5 Exchange Degeneracy and Identical Particles

In Sec. 15.2 we saw that in the independent particle model, the wavefunction

$$u_a(\mathbf{r}_1)\, u_b(\mathbf{r}_2) \tag{18}$$

is a solution of the Schrödinger equation corresponding to the energy $E = E_a + E_b$. Since the Schrödinger equation [Eq. (2)] is completely symmetrical in the two electrons, it is obvious that the wavefunction*

$$u_b(\mathbf{r}_1)\, u_a(\mathbf{r}_1) \tag{19}$$

is also a solution of the Schrödinger equation corresponding to the *same* eigenvalue $E_a + E_b$. Thus we have a degeneracy which is known as the *exchange degeneracy* because it arises due to the possibility of exchanging the two electrons**. We could also construct the linear combinations

$$u_+ = \frac{1}{\sqrt{2}}\left[u_a(\mathbf{r}_1)\, u_b(\mathbf{r}_2) + u_a(\mathbf{r}_2)\, u_b(\mathbf{r}_1) \right] \tag{20}$$

$$u_- = \frac{1}{\sqrt{2}}\left[u_a(\mathbf{r}_1)\, u_b(\mathbf{r}_2) - u_a(\mathbf{r}_2)\, u_b(\mathbf{r}_1) \right] \tag{21}$$

which are also solutions of Eq. (2) belonging to the same energy $E_a + E_b$; the factor $1/\sqrt{2}$ has been introduced so that the wavefunctions are normalized. The solutions u_+ and u_- are known as the symmetric and antisymmetric solutions because when the indices 1 and 2 are interchanged, u_+ remains the same whereas u_- changes sign. We will shortly see that it is essential that we use either the symmetrical or antisymmetrical solution rather than solutions given by Eqs. (18) and (19) which are neither symmetric nor antisymmetric. This is due to the indistinguishability of identical particles like electrons. It may be mentioned that in classical mechanics, identical particles are always distinguishable in the sense that it is possible to keep track of individual particles. However, in quantum mechanics, since it is not possible to keep track of individual particles (without disturbing the system), identical particles are indistinguishable. Thus considering a two electron system, if the two electrons are interchanged, we must get the same wavefunction except (possibly) for an unimportant phase factor***, i.e.

$$u(\mathbf{r}_1, \mathbf{r}_2) = e^{i\phi}\, u(\mathbf{r}_2, \mathbf{r}_1) \tag{22}$$

where ϕ is a real constant. Now, if P_{12} represents the particle interchange operator then

$$P_{12}\, u(\mathbf{r}_1, \mathbf{r}_2) = u(\mathbf{r}_2, \mathbf{r}_1) \tag{23}$$

*The wavefunction given by Eq. (18) corresponds to the state where the first electron is in the state *a* and the second electron in the state *b* whereas Eq. (19) corresponds to the first electron in state *b* and the second electron in state *a*.

**The exchange degeneracy exists as long as we neglect the electron-electron interaction. If the interaction between electrons is taken into account, the levels, in general, will split up (see Sec. 15.6).

***One could also argue that the probability of finding the first electron at $\mathbf{r}_1$ and the second electron at $\mathbf{r}_2$ must be equal to the probability of finding the first electron at $\mathbf{r}_2$ and the second electron at $\mathbf{r}_1$ giving

$$| u(\mathbf{r}_1, \mathbf{r}_2) |^2 = | u(\mathbf{r}_2, \mathbf{r}_1) |^2$$

which would lead to Eq. (22).

and $$P_{12}^2\, u(\mathbf{r}_1, \mathbf{r}_2) = P_{12}\, u(\mathbf{r}_2, \mathbf{r}_1) = u(\mathbf{r}_1, \mathbf{r}_2) \tag{24}$$

Further

$$\begin{aligned} P_{12}^2\, u(\mathbf{r}_1, \mathbf{r}_2) = P_{12}\, u(\mathbf{r}_2, \mathbf{r}_1) &= e^{-i\phi}\, P_{12}\, u(\mathbf{r}_1, \mathbf{r}_2) \\ &= e^{-i\phi}\, u(\mathbf{r}_2, \mathbf{r}_1) \\ &= e^{-2i\phi}\, u(\mathbf{r}_1, \mathbf{r}_2) \end{aligned}$$

Thus $e^{-2i\phi} = +1$ or $e^{i\phi} = \pm 1$ giving

$$u(\mathbf{r}_1, \mathbf{r}_2) = \pm\, u(\mathbf{r}_2, \mathbf{r}_1) \tag{25}$$

This equation shows that the wavefunction should be either symmetrical or antisymmetrical with respect to the interchange of the indices.

It may be mentioned that if the two particles are in the symmetric (or antisymmetric) state then they will remain in the symmetric (or antisymmetric) state for all times. This follows from the Schrödinger equation

$$\dot{\Psi} = \frac{1}{i\hbar} H \Psi \tag{26}$$

implying that $\dot{\Psi}$ has the same symmetry as Ψ [because H is always symmetrical with respect to the change of indices as the two electrons are identical; see, e.g., Eq. (1)]. Hence if $\Psi(\mathbf{r}_1, \mathbf{r}_2, t = 0)$ is symmetric then it will remain symmetric at Δt and so on.

15.6 The Pauli Exclusion Principle

Till now we have not considered the spin angular momentum associated with the electron. We denote the spin functions by $|\chi_\pm\rangle$ where $|\chi_+\rangle$ and $|\chi_-\rangle$ represent the spin up and spin down states*. For the two electron system, the spin functions are $|\chi_\pm(1)\rangle$ and $|\chi_\pm(2)\rangle$ where the numbers in the parenthesis refer to the first and second electron. Because of the indistinguishability of the electrons, we must construct appropriate linear combinations which are either symmetric or antisymmetric with respect to the interchange of indices; these states are denoted by

$$|\chi_t^+\rangle = |\chi_+(1)\chi_+(2)\rangle = |1\uparrow 2\uparrow\rangle \tag{27}$$

$$|\chi_t^-\rangle = |\chi_-(1)\chi_-(2)\rangle = |1\downarrow 2\downarrow\rangle \tag{28}$$

$$\begin{aligned} |\chi_t^0\rangle &= \frac{1}{\sqrt{2}}\Big[|\chi_+(1)\chi_-(2)\rangle + |\chi_-(1)\chi_+(2)\rangle\Big] \\ &= \frac{1}{\sqrt{2}}\Big[|1\uparrow 2\downarrow\rangle + |1\downarrow 2\uparrow\rangle\Big] \end{aligned} \tag{29}$$

$$\begin{aligned} |\chi_s\rangle &= \frac{1}{\sqrt{2}}\Big[|\chi_+(1)\chi_-(2)\rangle - |\chi_-(1)\chi_+(2)\rangle\Big] \\ &= \frac{1}{\sqrt{2}}\Big[|1\uparrow 2\downarrow\rangle - |1\downarrow 2\uparrow\rangle\Big] \end{aligned} \tag{30}$$

---

*Thus, if the electron is in the spin up (or spin down) state then the measurement of the z-component of the spin angular momentum will lead to $+\frac{1}{2}\hbar$ (or $-\frac{1}{2}\hbar$). At some places it will be convenient to designate the states $|\chi_+\rangle$ and $|\chi_-\rangle$ as $|\uparrow\rangle$ and $|\downarrow\rangle$ respectively.

the first three functions being symmetric and the last one being antisymmetric. The first function, for example, corresponds to both the functions being in the spin up state and so on.

Now, in Sec. 10.3 we had seen that the first three states (known as the triplet state) correspond to total spin $S = 1$ and the fourth state (known as the singlet state) corresponds to the total spin $S = 0$; in Eqs. (27)–(29), χ_t^+, χ_t^0 and χ_t^- correspond to $S = 1$ (with $m_s = 1, 0, -1$) and χ_s corresponds to $S = 0$.

We consider the ground state ($1s^2$) of the helium atom. The total wavefunction will be

$$u_{100}(\mathbf{r}_1)\, u_{100}(\mathbf{r}_2) \tag{31}$$

multiplied by the appropriate spin function. Now, it is an experimental fact that the ground state of the helium atom does not split up in a magnetic field; consequently it must be a singlet rather than a triplet state, i.e., we must have the following wavefunction representing the ground state

$$u_{100}(\mathbf{r}_1)\, u_{100}(\mathbf{r}_2)\, \frac{1}{\sqrt{2}}\Big[\,|\chi_+(1)\,\chi_-(2)\rangle - |\chi_-(1)\,\chi_+(2)\rangle\,\Big] \tag{32}$$

Thus the ground state wavefunction is antisymmetric*. Analysis of higher excited states of helium (and also of other atoms) shows that *the wavefunction for a system of electrons must be antisymmetric with respect to the interchange of two electrons*. Consequently, if the space dependent function is symmetric then the spin function should be antisymmetric and *vice versa*. The general wavefunction (for a 2 electron system) should therefore be of the form

$$\psi = \frac{1}{\sqrt{2}}\Big[\,\psi_a(1)\,\psi_b(2) - \psi_b(1)\,\psi_a(2)\,\Big] \tag{33}$$

where the subscripts a and b include the spin state, i.e., they represent n, l, m and m_s. It is obvious that if $a = b$ (i.e., if both the electrons have the same set of values of n, l, m and m_s) then

$$\psi = 0$$

which is the Pauli exclusion principle** according to which in an atom no two electrons can have the same set of values of the four quantum numbers n, l, m and m_s. Thus the antisymmetric nature of the total wavefunction leads automatically to the Pauli exclusion principle.

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*The ground state is denoted by ${}^1S_0$. The superscript 1 denotes a singlet (total spin=0). S denotes $L = 0$, the subscript 0 is to indicate $J = 0$. It is unfortunate that an S state here may be confused with total spin; certain conventions have to be adhered to, however!

**At this stage it may be worthwhile to mention that Pauli had put forward the exclusion principle before Uhlenbeck and Goudsmidt had introduced the idea of the spinning electron. In order to give satisfactory explanations of the spectra of alkali atoms and of the anomalous Zeeman effect, Pauli argued that for a general classification of each of the electron in an atom, four quantum numbers are needed. In his Nobel lecture, Pauli mentions that 'I proposed the assumption of a new quantum theoretic property of the electron. which I called *a two valuedness not describable classically*'. He then put forward his exclusion principle according to which there can never be two or more equivalent electrons in an atom which have the same values of all four quantum numbers. Pauli in his Nobel lecture also mentions that 'the physicists found it difficult to understand the exclusion principle, since no meaning in terms of a model was given to the fourth degree of freedom of the electron. The gap was filled by Uhlenbeck and Goudsmidt's idea of the electron spin which made it possible to understand the anomalous Zeeman effect simply by assuming that the spin quantum number of one electron is ½ and that the quotient of the magnetic moment to the mechanical angular moment has for the spin a value twice as large as for the ordinary orbit of the electron'. For a nice discussion on the historical development, the reader is referred to Ter Haar (1967) and Jammer (1966); the original article of Pauli has been reprinted in Ter Haar's book.

For a system of N electrons, the antisymmetric wavefunction is given by the Slater determinant

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{a_1}(1)\,\psi_{a_1}(2)\,\ldots\ldots & \psi_{a_1}(N) \\ \psi_{a_2}(1)\,\psi_{a_2}(2)\,\ldots\ldots & . \\ \cdot \quad\quad \cdot & \cdot \\ \cdot \quad\quad \cdot & \cdot \\ \cdot \quad\quad \cdot & \cdot \\ \psi_{a_N}(1) \quad \ldots\ldots & \psi_{a_N}(N) \end{vmatrix} \tag{34}$$

It is immediately obvious that if $a_1 = a_2$ then the two rows would become the same and the determinant would vanish.

Particles that are described by antisymmetric wavefunctions are known as Fermions and they are said to obey Fermi-Dirac statistics; examples of such particles are electrons, protons, neutrons, etc. On the other hand, particles which are described by symmetric wavefunctions are known as *Bosons* and they obey Bose-Einstein statistics; examples of such particles are photons, pions, etc. Pauli has proved that particles with half integral spins are Fermions and particles with integral spins are Bosons; the proof is, however, much beyond the scope of this book.

15.7 Excited States of Helium*

For the first excited state, we have the possible configurations 1*s* 2*s* and 1*s* 2*p*. Once again, if we ignore the electron-electron interaction, we have the independent particle model and the spatial part of the wavefunctions would be of the form

$$u_{100}(\mathbf{r}_1)\, u_{2l0}(\mathbf{r}_2) \tag{35}$$

where $l = 0$ for 2*s* and $l = 1$ for 2*p* states. This wavefunction, however, does not have the symmetry property required and the correct combinations are

$$u_+ = \frac{1}{\sqrt{2}}\left[u_{100}(\mathbf{r}_1)\, u_{2l0}(\mathbf{r}_2) + u_{100}(\mathbf{r}_2)\, u_{2l0}(\mathbf{r}_1)\right] \tag{36}$$

and

$$u_- = \frac{1}{\sqrt{2}}\left[u_{100}(\mathbf{r}_1)\, u_{2l0}(\mathbf{r}_2) - u_{100}(\mathbf{r}_2)\, u_{2l0}(\mathbf{r}_1)\right] \tag{37}$$

(For the ground state $1s^2$ configuration, u_- would vanish identically).

---

*The ground state of lithium and the corresponding exchange correction has been discussed by Flugge (1971).

We now incorporate spin wavefunctions. We have already seen that the singlet state $| \chi_s \rangle$ is antisymmetric and the triplet state $| \chi_t \rangle$ is symmetric [see Eqs. (27)–(30)]. In accordance with the exclusion principle, only the following antisymmetric combinations are permissible

$$\psi_s = u_+ \, | \chi_s \rangle \qquad \text{(singlet)} \qquad (38)$$

$$\psi_t = u_- \, | \chi_t \rangle \qquad \text{(triplet)} \qquad (39)$$

where the subscripts s and t refer to the singlet and triplet states respectively. Now, if we ignore the interaction of the electrons, these four states are degenerate; its inclusion lifts the degeneracy. Qualitatively, we can see this as follows. For a space symmetric wavefunction, there is a considerable probability for the two electrons to come close together (i.e., u_+ can be large for $\mathbf{r}_1 \approx \mathbf{r}_2$) whereas for the space antisymmetric state, this probability is quite small. Thus, the repulsive energy of the two electrons gives a larger positive contribution for u_+ than for u_-. One, therefore, expects triplet states to lie lower than the singlet ones. We must emphasize that this difference in energy is *not* due to spin dependent forces but is a consequence of the exclusion principle and the electrostatic interaction of the two electrons.

The configuration $1s2s$ gives the singlet state $^1S_0$ and the triplet $^3S_1$ since we have $L = 0$ and $S = 0$ or 1, the subscript gives the J value. One can estimate the difference in their energies by a perturbation calculation. The first order correction to their energy is

$$\Delta E_s = \iint u_+^* \frac{e^2}{r_{12}} u_+ \, d\tau_1 \, d\tau_2 \qquad \text{(singlet)} \qquad (40)$$

$$\Delta E_t = \iint u_-^* \frac{e^2}{r_{12}} u_- \, d\tau_1 \, d\tau_2 \qquad \text{(triplet)} \qquad (41)$$

where

$$r_{12} = | \mathbf{r}_1 - \mathbf{r}_2 | = \mathbf{r}_{21}$$

Since*

$$\langle \chi_s | \chi_s \rangle = 1 = \langle \chi_t | \chi_t \rangle \qquad (42)$$

and since e^2/r_{12} does not involve spin, only the space part of the wavefunction appears in the perturbation calculation. Next, we substitute for u_+ and u_- [from Eqs. (36) and (37) with $l = 0$] in Eqs. (40) and (41) to obtain

$$\Delta E_s = J_0 + K_0 \qquad (43)$$

$$\Delta E_t = J_0 - K_0 \qquad (44)$$

where

$$J_l = e^2 \iint u_{100}^* (\mathbf{r}_1) \, u_{2l0}^* (\mathbf{r}_2) \frac{1}{r_{12}} u_{100} (\mathbf{r}_1) \, u_{2l0} (\mathbf{r}_2) \, d\tau_1 \, d\tau_2 \qquad (45)$$

and

$$K_l = e^2 \iint u_{100}^* (\mathbf{r}_1) \, u_{2l0}^* (\mathbf{r}_2) \frac{1}{r_{12}} u_{100} (\mathbf{r}_2) \, u_{2l0} (\mathbf{r}_1) \, d\tau_1 \, d_2 \, \tau_2 \qquad (46)$$

---

*It is because of the relation $\langle \chi_s | \chi_s \rangle = 1$ that the perturbation to the ground state energy will be simply Eq. (11) although the ground state wavefunction is given by Eq. (32).

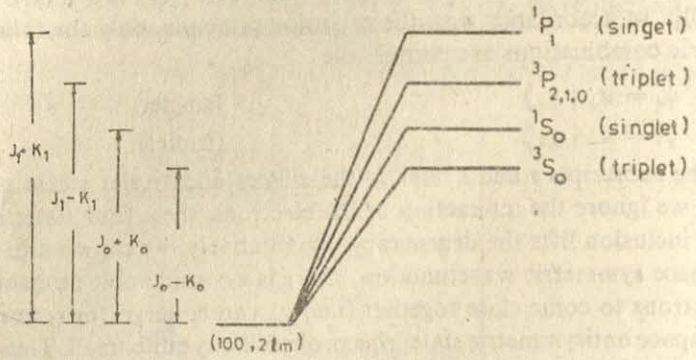

Fig. 15.2 The splitting of the first excited state of the helium atom.

and in arriving at Eqs. (43) and (44) we have used the fact that in the integrals J_l and K_l, we can interchange $\mathbf{r}_1$ and $\mathbf{r}_2$.

The integral J_1 (for $l = 0$) is of the same type as we had encountered in the ground state energy shift calculation; the term K_l is known as the 'exchange' integral. The evaluation is tedious but straightforward and yields

$$J_0 \approx 9.1 \text{ eV} \quad \text{and} \quad K_0 \approx 0.4 \text{ eV} \tag{47}$$

A similar treatment can be given for the $1s2p$ configuration. Since $l_1 = 0$ and $l_2 = 1$, $L = 1$ and for the singlet state ($S = 0$) J takes the value 1; on the other hand, for the triplet state ($S = 1$) J takes the values 2, 1, 0. Thus the possible states are

$$^1P_1 \quad \text{and} \quad ^3P_{2,1,0}$$

Again the triplet levels lie lower than the singlet state; in fact

$$J_1 \approx 10.2 \text{ eV} \quad \text{and} \quad K_1 \approx 0.1 \text{ eV} \tag{48}$$

The corresponding energy levels are given in Fig. 15.2 (see also Problem 15.4).

15.8 Fine Structure

In order to remove the degeneracy within the triplet levels, it is necessary to include the spin orbit interaction. This is the interaction between the magnetic moment (associated with spin) and the orbital motion of the electron and is represented by a term of the form*

$$\sum_i \xi(r_i)\, \mathbf{L} \cdot \mathbf{S} \tag{49}$$

in the Hamiltonian. For a state with a particular value of L, S and J, we have

$$\langle \mathbf{L} \cdot \mathbf{S} \rangle = \frac{1}{2}\Big[J(J+1) - L(L+1) - S(S+1)\Big] \tag{50}$$

which gives, 1, -1 and -2 for the $^3P_2$, $^3P_1$, and $^3P_0$ states respectively. Writing

---

*L, S are the orbital and spin quantum numbers of the atom.

$$2\Gamma = \int d\tau\, \psi^* \Big(\sum_i \xi(r_i) \Big)\, \psi \tag{51}$$

we have, for the spin orbit correction, 2Γ, -2Γ and -4Γ for the above three terms giving the so-called fine structure splitting which is $\sim 10^{-4}$ eV. Finally, it may be pointed out that there is a further $2J+1$ degeneracy in each of these terms which can be removed by the application of a magnetic field. The total number of ${}^3P$ states is $5 + 3 + 1 = 9$; this is $(2S+1)(2L+1)$ as may be expected.

15.9 Helium Spectra

In order to compare the foregoing theory with experiment, we have to state the rules governing the transitions between the various states. In the dipole approximation (to be discussed in Secs. 21.3 and 22.4), it can be shown that no transition occurs between singlet and triplet states. As a result, the energy level diagram of helium splits into two parts as shown in Fig. 15.3. The figure shows the energy levels when one of the electrons is in the $1s$ state and the other in nl state. Note the following features:

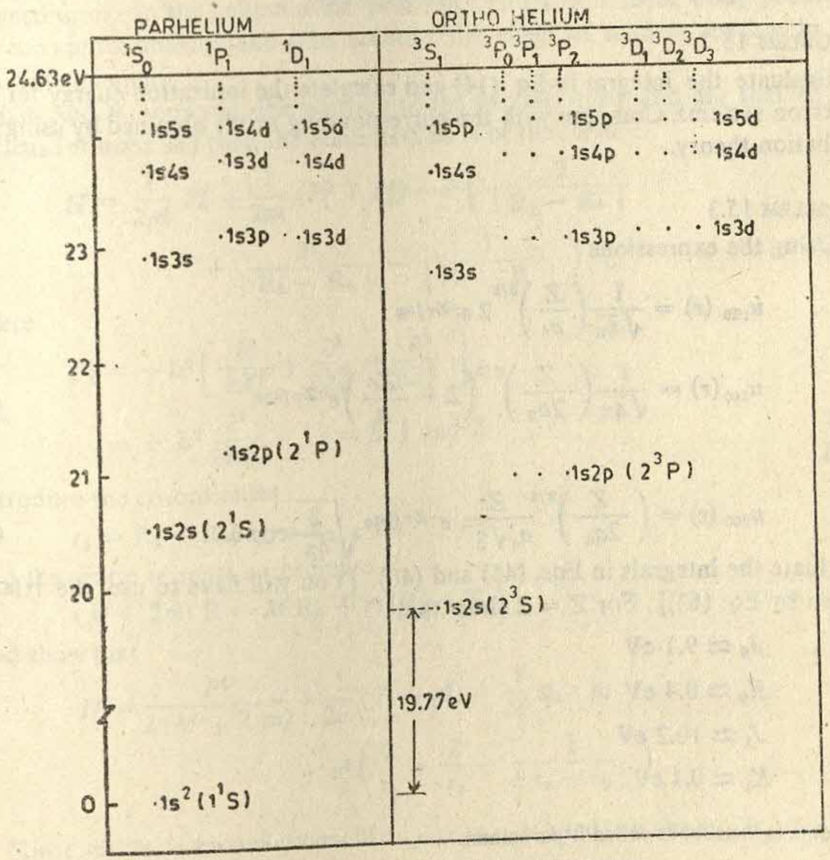

Fig. 15.3 The energy levels of the helium atom.

(1) Singlet levels, belonging to a particular value of n and l have higher energy than triplet levels of the same n and l.

(2) For $n = 2$, the difference $^1S - {}^3S$ is larger than the $^1P - {}^3P$ difference. This is because the exchange integral K for the P state is smaller; there is a smaller contribution from those regions where $1/r_{12}$ is large.

(3) The states $2\,{}^3S$ and $2\,{}^1S$ are *metastable*. The $2\,{}^1S \rightarrow 1\,{}^1S$ transition is forbidden because of the selection rule $\Delta l = \pm 1$ for dipole transitions and the $2\,{}^3S \rightarrow 1\,{}^1S$ for this reason as well as the one mentioned earlier, forbidding triplet-singlet transitions. Thus helium exists as two 'gases' as it were, parahelium* atoms with $S = 0$ and orthohelium with $S = 1$.

PROBLEMS

Problem 15.1

Evaluate the integral in Eq. (11) and calculate the ground state energy of two electron systems like He, Li$^+$, Be^{++} and B^{+++}. Determine the ionization energy and compare with the corresponding experimental values which are 24.63 eV, 75.64 eV, 153.87 eV, and 259.31 eV respectively.

Problem 15.2

Evaluate the integral in Eq. (14) and calculate the ionization energy for two electron systems. Compare with the corresponding result obtained by using perturbation theory.

Problem 15.3

Using the expressions

$$u_{100}(\mathbf{r}) = \frac{1}{\sqrt{4\pi}}\left(\frac{Z}{a_0}\right)^{3/2} 2\,e^{-Zr/a_0} \tag{52}$$

$$u_{200}(\mathbf{r}) = \frac{1}{\sqrt{4\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0} \tag{53}$$

and

$$u_{200}(\mathbf{r}) = \left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0\sqrt{3}}\,e^{-Zr/2a_0}\sqrt{\frac{3}{4\pi}}\cos\theta \tag{54}$$

evaluate the integrals in Eqs. (45) and (46). [You will have to use the relation given by Eq. (63)]. For $Z = 2$ show that

$J_0 \approx 9.1$ eV

$K_0 \approx 0.4$ eV

$J_1 \approx 10.2$ eV

$K_1 \approx 0.1$ eV

---

*Some earlier books called it parhelium.

PROBLEM 15.4

Using the values of J_0, K_0, J_1 and K_1 obtained in Problem 15.3 draw the energy levels of the $1s2s$ and $1s2p$ states of helium atom (see Fig. 15.2) and calculate the ionization energies of the corresponding states.

PROBLEM 15.5

In the independent particle model (see Sec. 15.2), the first excited state of the helium atom is 8-fold degenerate* (we are neglecting spin). In order to evaluate the electron interaction energy $\langle e^2/r_{12} \rangle$ we must choose a representation in which the perturbation is diagonal. Show that, in order to make $H'(=e^2/r_{12})$ diagonal, we must choose the appropriate symmetric and antisymmetric forms [see Eqs. (36) and (37)].
(Pauling and Wilson (1935) have explicitly shown this by solving an 8×8 determinant.)

PROBLEM 15.6

(a) In the hydrogen atom problem we had shown that the two body problem can be reduced to a one body problem with electron mass replaced by the reduced mass. In the helium atom problem (which is a three body problem) one can approximately take into account the effect of nuclear motion in the following manner.

If $\mathbf{R}_1$ and $\mathbf{R}_2$ represent the position of the two electrons and $\mathbf{R}_n$ that of the nucleus (of mass M) then the Hamiltonian is of the form

$$H = \frac{1}{2M} P_n^2 + \frac{1}{2m} (P_1^2 + P_2^2) - e^2 \left(\frac{2}{|\mathbf{R}_1 - \mathbf{R}_n|} + \frac{2}{|\mathbf{R}_2 - \mathbf{R}_n|} - \frac{1}{|\mathbf{R}_1 - \mathbf{R}|} \right) \tag{55}$$

where

$$P_i^2 = -\hbar^2 \left[\frac{\partial^2}{\partial X_i^2} + \frac{\partial^2}{\partial Y_i^2} + \frac{\partial^2}{\partial Z_i^2} \right] = -\hbar^2 \frac{\partial^2}{\partial \mathbf{R}_i^2} \qquad i = n, 1 \text{ and } 2 \tag{56}$$

Introduce the co-ordinates

$$\mathbf{r}_1 = \mathbf{R}_1 - \mathbf{R}_n, \; \mathbf{r}_2 = \mathbf{R}_2 - \mathbf{R}_n \tag{57}$$

and the centre of mass co-ordinate $\mathbf{R}$

$$(M + 2m)\, \mathbf{R} = M\, \mathbf{R}_n + m(\mathbf{R}_1 + \mathbf{R}_2) \tag{58}$$

and show that

$$H = \frac{P^2}{2(M + 2m)} + \frac{1}{2\mu}(p_1^2 + p_2^2) + \frac{1}{M} \mathbf{p}_1 \cdot \mathbf{p}_2 + e^2 \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \tag{59}$$

---

*There will be four wavefunctions like $u_{100}(\mathbf{r}_1) u_{2lm}(\mathbf{r}_2)$ and four like $u_{2lm}(\mathbf{r}_1)\, u_{100}(\mathbf{r}_2)$.

where

$$\mu = \frac{mM}{m + M} \tag{60}$$

is the reduced mass of an electron with the nucleus. Since $M \gg \mu$ the term $(1/M)$ $\mathbf{p}_1 \cdot \mathbf{p}_2$ will be small in comparison to the preceding term and in the first approximation can be neglected. In this approximation, the resulting Hamiltonian is of the same form as Eq. (1) except for m being replaced by μ and for an additional term involving the translational motion of the centre of mass.

(b) Use first order perturbation theory to show that using a wavefunction of the form given by Eq. (3), the effect of the term $(1/M)\,\mathbf{p}_1 \cdot \mathbf{p}_2$ is zero.

SOLUTIONS

SOLUTION 15.1

The normalized hydrogen atom ground state wavefunction is given by Eq. (52). Thus

$$u_{100}(\mathbf{r}_1)\, u_{100}(\mathbf{r}_2) = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \exp\left[-Z\frac{(r_1 + r_2)}{a_0}\right] \tag{61}$$

Substituting in Eq. (11) we get

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{Z^6 e^2}{\pi^2 a_0^6} \int d\tau_1 e^{-2Zr_1/a_0} \int d\tau_2 e^{-2Zr_2/a_0} \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{62}$$

Now

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \begin{cases} \dfrac{1}{r_1} \displaystyle\sum_l \left(\frac{r_2}{r_1}\right)^l P_l(\cos\theta) & \text{for } r_1 \geqslant r_2 \\[2ex] \dfrac{1}{r_2} \displaystyle\sum_l \left(\frac{r_1}{r_2}\right)^l P_l(\cos\theta) & \text{for } r_2 \geqslant r_1 \end{cases} \tag{63}$$

where θ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$ [see, e.g., Irving and Mullineux (1959), p. 176]. Further, in evaluating the second integral, if we choose the z_2-axis along $\mathbf{r}_1$, then

$$d\tau_2 = r_2^2 \, dr_2 \sin\theta \, d\theta \, d\varphi$$

Introducing

$$\rho_1 = \frac{2Zr_1}{a_0} \quad \text{and} \quad \rho_2 = \frac{2Zr_2}{a_0}$$

we get

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \frac{Ze^2}{32\,\pi^3 a_0} \iiint \rho_1^2 d\rho_1 \sin\theta_1\, d\theta_1\, d\varphi_1 e^{-\rho_1} \left[\frac{1}{\rho} \int_0^{\rho_1} \rho_2^2\, d\rho_2\, e^{-\rho_2} \right.$$

$$\times \frac{1}{\rho_1} \sum_l \left(\frac{\rho_2}{\rho_1} \right)^l \iint P_l(\cos\theta) \sin\theta\, d\theta\, d\varphi + \int_{\rho_1}^{\infty} \rho_2^2\, d\rho_2\, e^{-\rho_2}$$

$$\left. \times \frac{1}{\rho_2} \sum_l \left(\frac{\rho_1}{\rho_2} \right)^l \iint P_l(\cos\theta) \sin\theta\, d\theta\, d\varphi \right]$$

$$= \frac{Ze^2}{8\pi a_0} \iiint \rho_1^2\, d\rho_1 \sin\theta_1\, d\theta_1\, \varphi_1\, e^{-\rho_1} \left[\frac{1}{\rho_1} \int_0^{\rho_1} \rho_2^2\, e^{-\rho_2}\, d\rho_2 \right.$$

$$\left. + \int_{\rho_1}^{\infty} \rho_2\, e^{-\rho_2}\, d\rho_2 \right]$$

$$= \frac{5}{8} Z \frac{e^2}{a_0} = \frac{5Z}{4} E_H \qquad (64)$$

where we have used the relation

$$\int_0^{\pi} P_l(\cos\theta) \sin\theta\, d\theta = 2 \quad \text{for } l = 0 \qquad (65)$$

$$= 0 \quad \text{for } l \geqslant 1$$

Thus, according to the first order perturbation theory, the ground state energy is given by

$$W^{(1)} = -2Z^2 E_H + \frac{5}{4} Z E_H = \left(-Z^2 + \frac{5}{8} Z \right) 2\, E_H$$

$$= \left(-Z^2 + \frac{5}{8} Z \right) \times 27.21 \text{ eV} \qquad (66)$$

The calculated values are tabulated in Table 15.1. Since the ground state energy of a one electron atom is $-Z^2 E_H$, the ionization energy is given by

$$\left[\left(Z^2 - \frac{5}{8} Z \right) 2\, E_H - Z^2 E_H \right] = \left[Z^2 - \frac{5}{4} Z \right] E_H \qquad (67)$$

In Table 15.1 we have tabulated the ionization energy as given by the above equation and compared with the corresponding experimental values. It is interesting to note that the absolute error remains almost the same; however, the

TABLE 15.1

GROUND STATE AND IONIZATION ENERGIES OF TWO ELECTRON ATOMS

Atom	*Z*	*Ground State Energy using Perturbation Theory* [Eq. (66)]	*Ionization Energy* *Experimental value*	*Ionization Energy* *Perturbation Theory* [Eq. (67)]	*Ionization Energy* *Variational Method* [Eq. (73)]	*Difference between Experimental Values and Perturbation Theory Results for Ionization Energy*
He	2	—74.83 eV	24.63 eV	20.40 eV	23.06 eV	4.23 eV
Li+	3	—193.87 eV	75.64 eV	71.43 eV	74.08 eV	4.21 eV
Be++	4	—367.3 eV	153.87 eV	149.66 eV	152.31 eV	4.21 eV
B+++	5	—595.2 eV	259.31 eV	255.09 eV	257.75 eV	4.22 eV

percentage error decreases with increase in Z. Physically this is due to the fact that for large Z, the term $-Ze^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$ would dominate over the term e^2/r_{12}.

SOLUTION 15.2

Since exp $[-Z'r/a_0]$ is the ground state wavefunction for a hydrogen like atom with charge $Z'e$, we must have

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2-\frac{Z'e^2}{r_1}\right]\phi(\mathbf{r}_1,\mathbf{r}_2)=-Z'^2E_H\phi(\mathbf{r}_1,\mathbf{r}_2) \tag{68}$$

Thus

$$E(Z')=\iint\overset{*}{\phi}\left[-2Z'^2E_H+(Z'-Z)e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right)+\frac{e^2}{r_{12}}\right]\phi\,d\tau_1\,d\tau_2 \tag{69}$$

Now

$$e^2\iint\overset{*}{\phi}\left(\frac{1}{\mathbf{r}_1}+\frac{1}{\mathbf{r}_2}\right)\phi\,d\tau_1\,d\tau_2=2e^2\iint\frac{|\phi|^2}{\mathbf{r}_1}\,d\tau_1\,d\tau_2$$

$$=2Z'\frac{e^2}{a_0}=4Z'E_H \tag{70}$$

and

$$\iint\overset{*}{\phi}\,\frac{e^2}{r_{12}}\,\phi\,d\tau_1\,d\tau_2=\frac{5}{4}Z'E_H \tag{71}$$

[see Eq. (64)]. On substitution we get Eq. (15) and the condition $dE/dZ'=0$ leads to

$$Z'=Z_{\text{eff}}=Z-\frac{5}{16}$$

Thus the ground state energy is

$$E = -2\left(Z - \frac{5}{16}\right)^2 E_H \tag{72}$$

and the corresponding ionization energy is

$$\left[2\left(Z - \frac{5}{16}\right)^2 - Z^2\right] E_H \tag{73}$$

which gives a much better estimate than the perturbation theory result (see Table 15.1).

SOLUTION 15.4

According to the first order perturbation theory the energy levels for the 1*s* 2*s* and 1*s*2*p* configurations are given by

$$\begin{aligned} W^{(1)} &= \left(-Z^2 E_H - \frac{Z^2}{4} E_H\right) + J_l \pm K_l \\ &= -5\,E_H + J_l \pm K_l \end{aligned} \tag{74}$$

where we have assumed $Z = 2$ and the upper and lower states correspond to singlet (parahelium) and triplet (orthohelium) states respectively. Substituting the values we get

$$\begin{aligned} W^{(1)}_{1s2s} &\approx -58.9 \pm 0.4 \text{ eV} \\ &\approx -58.5 \text{ eV and } -59.3 \text{ eV} \end{aligned} \tag{75}$$

$$\begin{aligned} W^{(1)}_{1s2p} &\approx -57.8 \pm 0.1 \text{ eV} \\ &\approx -57.7 \text{ eV and } -57.9 \text{ eV} \end{aligned} \tag{76}$$

The ionization energies are given by

$$\left.\begin{aligned} -Z^2 E_H - W^{(1)} &\approx 4.1 \text{ eV for the } 1s\ 2s \text{ parahelium state } ({}^1S_0) \\ &\approx 4.9 \text{ eV for the } 1s\ 2s \text{ orthohelium state } ({}^3S_0) \\ &\approx 3.3 \text{ eV for the } 1s\ 2p \text{ parahelium state } ({}^1P_1) \\ &\approx 3.5 \text{ eV for the } 1s\ 2p \text{ orthohelium state } ({}^3P_{2,1,0}) \end{aligned}\right\} \tag{77}$$

The corresponding experimentals values are 3.97 eV, 4.76 eV, 3.368 eV and 3.623 eV respectively.

CHAPTER SIXTEEN

Many Electron Atoms

16.1 Introduction

As we have seen, in the case of the helium atom, exact solutions are not possible even for two electron atoms. However, one can resort to useful approximations depending on just which terms in the Hamiltonian can be assumed small. We must then not be surprised if these approximations differ as we go from light to heavy atoms. In this chapter we shall discuss the central field approximation and describe the L-S or Russell-Saunders coupling scheme applicable particularly to light atoms. Then we go on to consider, briefly, j-j coupling which is useful for heavier atoms although pure examples of it do not occur very frequently.

16.2 The Central Field Approximation

A suitable Hamiltonian which takes into account the mutual interaction of the electrons as well as the spin orbit interaction is

$$H = \sum_{i=1}^{Z}\left[-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i} + \xi(r_i)\,\mathbf{l}_i.\mathbf{s}_i\right] + \sum_{i<j}\frac{e^2}{r_{ij}} \tag{1}$$

In Sec. 18.5 it will be shown that for a single electron, the spin orbit interaction has the form $\xi(r)\mathbf{l}.\mathbf{s}$ and the above is a simple generalization. In the last term representing the electrostatic interaction between pairs of electrons, the injunction $i < j$ is to prevent double counting.

To begin with, we ignore the last two terms in which case the solution of the Schrödinger equation is trivial. However, it is a very poor approximation as we have seen in the case of helium (see Chapter 15). Indeed, the effect of each electron there was to reduce the effective nuclear charge, changing it from 2 to 1.69.

We therefore seek to include the electrostatic term by assuming that each electron moves in an average central field due not only to the nucleus but the other electrons as well. We can have an idea of the sort of potential we want by appealing to a classical picture. When the ith electron is very close to the nucleus and the other $Z - 1$ form a shell of charges outside, we expect the potential energy to be $-Ze^2/r_i$ + constant. For large r_i, on the other other hand, the $Z - 1$ electrons effectively shield the nucleus and the potential energy approaches $-e^2/r_i$; i.e.,

$$\begin{aligned}\overline{V} &\to -\frac{Ze^2}{r_i} + \text{constant, for small } r_i\\ &\to -e^2/r_i \quad \text{for large } r_i\end{aligned} \tag{2}$$

Such an approximation is known as the central field approximation.

In a system of several interacting electrons, one cannot talk about the state of each electron separately. However, the central field approximation permits us this luxury and we can assign quantum numbers n, l, m_l, m_s, j and m to each electron*. Since, however, the potential in which each electron moves is not of a Coulomb type, the energies will depend on n and l.

16.3 Wave Functions

The Schrödinger equation in the central field is

$$\{\Sigma[T_i + \bar{V}(r_i)]\}\,\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) = E\,\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) \tag{3}$$

where T_i is the kinetic energy operator for the ith electron. The wave function Ψ can be written as a product of solutions $\Psi_i(\mathbf{r}_i)$ and Eq. (3) is then separable into Z equations of the type

$$[T_i + \bar{V}(r_i)]\,\Psi_i(\mathbf{r}_i) = E_i\,\Psi_i(r_i) \tag{4}$$

Since $\bar{V}$ is independent of angles, the solutions are of the form

$$\Psi_i = R_{n_i\, l_i}(r_i)\; Y_{l_i,\, m_i}(\theta_i, \varphi_i) \tag{5}$$

where n_i, l_i and m_i are the usual quantum numbers (see Sec. 5.3) associated with the ith particle. The state of the atom as a whole, is specified by assigning these quantum numbers to each electron. If we include spin, then the component of the spin m_s ($= \pm \frac{1}{2}$) also has to be specified.

The Pauli exclusion principle demands that the entire wavefunction be antisymmetric under the exchange of co-ordinates and spin of any pair of electrons (see Sec. 15.6). This means that no two electrons can have the same quantum numbers. Formally, antisymmetry is satisfied by the Slater determinant

$$\Psi = \begin{vmatrix} \Psi\alpha_1(q_1) & \Psi\alpha_1(q_2) & \cdots & \Psi\alpha_1(q_Z) \\ \Psi\alpha_2(q_1) & \Psi\alpha_2(q_2) & \cdots & \Psi\alpha_2(q_Z) \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \Psi\alpha_Z(q_1) & \Psi\alpha_Z(q_2) & \cdots & \Psi\alpha_Z(q_Z) \end{vmatrix} \tag{6}$$

Here $\Psi\alpha_i(q_j)$ is the wavefunction describing the jth electron in the set of quantum numbers α_i and q_j stands for the coordinates and spin of the jth electron. It can be seen that interchange of two columns corresponds to interchanging two electrons and will change the sign of Ψ. If two rows are the same (i.e., states are the same), Ψ vanishes.

A particular term in Eq. (6), for example, is $\psi_{\alpha_8}(q_1)\,\psi_{\alpha_6}(q_2), \ldots, \psi_{\alpha_3}(q_Z)$ which corresponds to the first electron in state α_8, the second in α_6, etc; there will also be a term $\psi_{\alpha_6}(q_1)\,\psi_{\alpha_8}(q_2)\ldots$ corresponding to the first electron in state α_6 and the second in α_8, etc. Indeed there will be a term placing each electron in every state of the set $\alpha_1, \ldots, \alpha_Z$. This means that one cannot assign a particular electron to a particular state. Nevertheless, it is convenient to talk of electrons in the 1*s* state or 3*d* state, etc.

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*Here, m_s ($= \pm\frac{1}{2}$) is the eigenvalue of s_Z and m is the eigenvalue of j_Z.

16.4 Shells and Subshells

Electrons with the same principal quantum number *n* are said to occupy a particular *shell*. These hells are called *K*, *L*, *M*, *N*, *O*, etc. according as *n* equals 1, 2, 3, 4, 5, etc. The energy levels corresponding to different *l* but the same *n* value are called *subshells* belonging to that shell. Subshells corresponding to *l* values of 0, 1, 2, 3, etc. are called *s*, *p*, *d*, *f*, etc., the labels deriving from an old spectroscopic terminology—sharp, principal, diffuse and fundamental. Those electrons which have the same values of both *n* and *l* are called ***equivalent electrons***; the maximum number of equivalent electrons is $2(2l+1)$.

For example, the electronic configuration for the ground state of boron ($Z = 5$) is $1s^2\ 2s^2\ 2p$ meaning that the 1*s* and 2*s* subshells contain their full quota of electrons whereas the 2*p* contains just one electron. Similarly, carbon will be $1s^2\ 2s^2\ 2p^2$.

As *n* increases, the energy levels become more and more closely spaced. For large values of *n*, the shells overlap and the order of filling of the subshells depends upon *l* as well as on *n*. For example, vanadium ($Z = 23$) has the ground state $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$ which is usually abbreviated as (Ar) $4s^2\ 3d^3$ because the element argon (Ar) has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. We would expect chromium ($Z = 24$) to be in (Ar) $4s^2\ 3d^4$ but instead it has the configuration (Ar) $4s\ 3d^5$. The ground state electronic configuration of all the elements is discussed in books on atomic spectra; see, for example, White (1934).

16.5 Hartree's Method of Self Consistent Fields

An important method for obtaining a suitable central field is due to Hartree. In this method, a suitable function $\bar{V}(r_i)$ is first chosen with a property close to that given by Eq. (2). The single particle states ψ_i are then obtained by solving the Schrödinger equation. Now, the part of the potential due to all electrons *other than* the *i*th is calculated by assuming that each of these electrons yields a charge distribution as given by their wavefunctions already worked out.

Consider the *j*th electron, $j \neq i$. The average charge in a volume element $d\tau_j$ due to this electron is $e\,d\tau_j|\psi_j(r_j)|^2$ and the potential energy of interaction with the *i*th electron is

$$e^2 \int d\tau_j \frac{|\psi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{7}$$

Thus, the *i*th electron moves in a potential generated by all the other electrons, namely

$$e^2 \sum_{j \neq i} \int d\tau_j \frac{|\psi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

so that the full potential is

$$\overline{V}(r_i) = -\frac{Ze^2}{r_i} + e^2 \sum_{j=1}^{Z-1} \int d\tau_j \frac{|\psi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{8}$$

where the first term is due to the nucleus. With this potential, we can repeat the whole process, i.e., calculate the wavefunctions (in general, numerically), etc. The process is repeated until two successive iterations yield the same $\overline{V}(r_i)$ to the desired accuracy. In other words, the electrons are supposed to move in a potential which *they themselves generate*. This is why the method is called 'self consistent'.

The numerical calculations necessary are possible only with high speed computers and that too with a great deal of technical expertise. We shall, however, illustrate the method with an elementary calculation for helium. Hartree's method is designed for heavier atoms than helium but the purpose here is to clarify the general technique. We have used a small programmable calculator for this purpose and would strongly advise the student to try this calculation himself.

16.6 Application to Helium Atom

We start by assuming a potential*

$$V_0(r) = -2/r \tag{9}$$

This is the potential either electron moves in if the other were absent. [In practice, it would save considerable labour to *start* with a more realistic potential in accordance with Eq. (2)]. The radial function for the ground state is [see Eq. (51), Chapter 5]

$$R_{10}(r) = 2^{5/2} e^{-2r} \tag{10}$$

so that

$$\psi_{100}(\mathbf{r}_2) = R_{10}(r_2)\, Y_{00} = \frac{1}{\sqrt{4\pi}} R_{10}(r_2) \tag{11}$$

The suffix 2 indicates that it is in the field of the second electron that the first one moves. Next, we calculate the integral

$$\mathcal{J} = \int d\tau_2 \frac{|\psi_{100}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{12}$$

---

*We shall use atomic units, from hereon, for these calculations. In atomic units electron ma $m = 1$, the magnitude of the electronic charge $|e| = 1$ and $\hbar = 1$. Thus, in these unit Bohr radius is 1, the energy of the hydrogen atom 0.5 and the velocity of light is 137.

In high energy (particle) physics, it is customary to use another set of units with $\hbar = 1$ a $c = 1$.

using the same method as given in Solution 15.1. The result is

$$\mathcal{J} = \frac{1}{r_1}\left\{1 - (1 + 4r_1 + 8r_1^2)\, e^{-4r_1}\right\} + 2\,(1 + 4r_1)\, e^{-4r_1}$$

Adding the term $-Z/r_1$ [see Eq. (8)], we obtain

$$\bar{V}_1(r_1) = -\left\{\frac{1}{r_1} + \left(\frac{1}{r_1} + 2\, e^{-4r_1}\right)\right\} \tag{13}$$

the suffix on $\bar{V}_1$ indicating that we have now worked out the first iteration. Note that this function already has the correct limiting behaviour for $r_1 \ll 1$ and $r_1 \gg 1$.

We can solve the radial equation numerically to obtain the ground state wavefunction using the method given in Chapter 17. The normalized wavefunction $u(r)$, corresponding to an eigenvalue $E \approx 0.82$, is plotted in Fig. 16.1. Here $u(r) = rR(r)$ is the more convenient function to use. The radial equation is then

$$\frac{d^2u}{dr^2} = -2\,[E - V]\,u = F(r)\,u \tag{14}$$

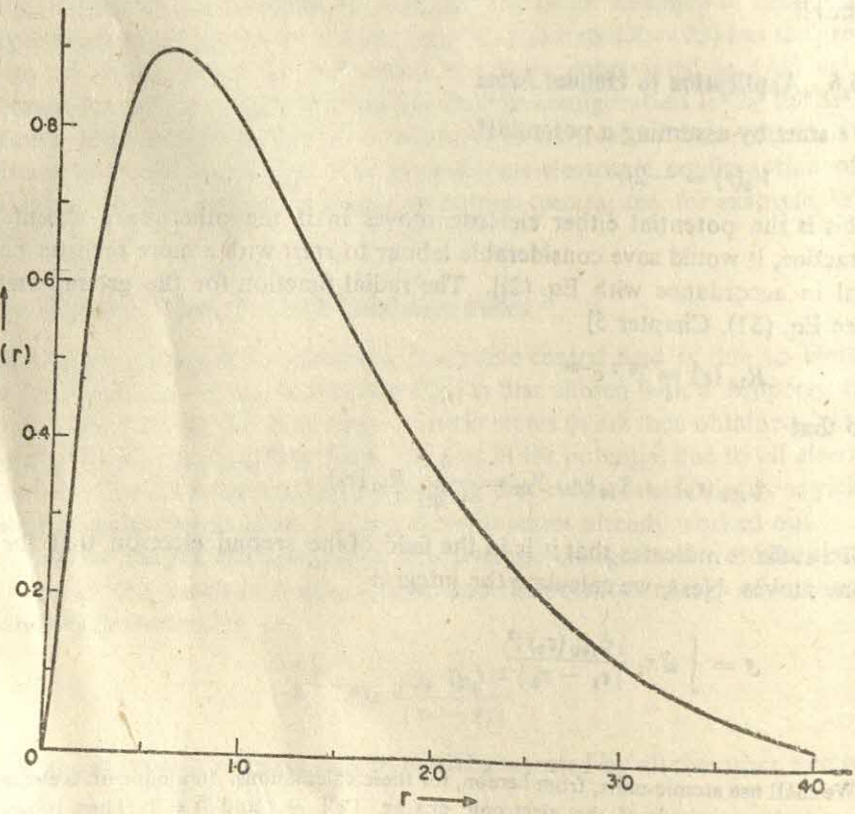

Fig. 16.1 The normalized wavefunction $u(r)$ corresponding to an eigenvalue $E \approx 0.82$.

and u is normalized to give

$$\int_0^\infty |u|^2 \, dr = 1$$

The energy of each election corresponding to this function is

$$\langle H \rangle = \left\langle -\tfrac{1}{2}\nabla^2 - \frac{2}{r} + \frac{1}{r_{12}} \right\rangle \tag{15}$$

where the three terms are the kinetic energy, the potential energy due to the nucleus and the energy of repulsion between the electrons. We write

$$\langle H \rangle = \langle t \rangle + \langle v \rangle + \langle v_{12} \rangle \tag{16}$$

Since there is no angular dependence for the s wave functions, we have

$$\langle \nabla^2 \rangle = \int_0^\infty u^* \frac{d^2u}{dr^2} \, dr \tag{17}$$

The simplest way to evaluate this is to use Eq. (14) and write

$$\langle t \rangle = -\frac{1}{2} \int_0^\infty F(r) \, u^2 \, dr \tag{18}$$

Similarly

$$\langle v \rangle = \int_0^\infty \frac{u^2}{r} \, dr \tag{19}$$

To evaluate $\langle v_{12} \rangle$, we write

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{1}{r_1} \sum_{l=0}^{\infty} \left(\frac{r_2}{r_1} \right)^l P_l(\cos\theta) \quad \text{for } r_2 < r_1 \\ &= \frac{1}{r_2} \sum_{l=0}^{\infty} \left(\frac{r_1}{r_2} \right)^l P_l(\cos\theta) \quad \text{for } r_2 > r_1 \end{aligned} \tag{20}$$

Since for the s wavefunctions only the $l = 0$ terms survive on integration over angles, we have

$$\left\langle \frac{1}{r_{12}} \right\rangle = \int_0^\infty |u(r_1)|^2 \, dr_1 \left\{ \frac{1}{r_1} \int_0^{r_1} |u(r_2)|^2 \, dr_2 + \int_{r_1}^\infty \frac{|u(r_2)|^2}{r_2} \, dr_2 \right\} \tag{21}$$

Each of the integrals in Eqs. (18), (19) and (21) has to be evaluated numerically. For the wavefunction in Fig. 16.1, we obtain

$$\langle t \rangle = 1.29$$
$$\langle v \rangle = -3.20 \tag{22}$$

and

$$\langle v_{12} \rangle = 0.97$$

The total energy of helium atom (ground state) is not twice the sum of the above values. We must remember that the electrostatic energy of the two electrons must be added just once. Thus

$$E_0 = 2(\langle t \rangle + \langle v \rangle) + \langle v_{12} \rangle \approx -2.85 \tag{23}$$

which turns out to be -77.6 eV; somewhat larger than the observed value of -79 eV.

The above calculation, chosen for its simplicity, misses some of the subtler points. For example, the two electrons in the ground state are both in the 1*s* state so that the self-consistent potential for them is the same. This, however, is not true in general. For the 1*s* 2*s* configuration of helium, we shall have, for the potential of one of the electrons due to the other,

$$V_1(r_1) = -\frac{2}{r_1} + \int d\tau_2 \frac{|\psi_{2s}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{24}$$

and

$$V_2(r_2) = -\frac{2}{r_2} + \int d\tau_1 \frac{|\psi_{1s}(\mathbf{r}_1)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{25}$$

showing explicitly that $V_1(r_1)$ and $V_2(r_2)$ are different functions. (Hence the suffixes on V_1 and V_2). One can use these to calculate energies as before.

Since the effective Hamiltonians for the various electrons are different, the resulting solutions of the wave equations for the electrons will not, in general, be orthogonal. Moreover, the wavefunctions used will have to satisfy the exclusion principle. These features are incorporated in the Hartree-Fock method. The computations, however, are more formidable and certain modified versions of the method are sometimes more convenient; for further details see, e.g., Herman and Skillman (1963).

16.7 Coupling Schemes

We now include the spin orbit interaction so that the potential reads

$$V = V' + V_{so} \tag{26}$$

where

$$V' = -Ze^2 \sum_i \frac{1}{r_i} + e^2 \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{27}$$

and

$$V_{so} = \sum \xi(r_i)\, \mathbf{l}_i \cdot \mathbf{s}_i \tag{28}$$

We can rewrite V as

$$V = V_c + v + V_{so} \tag{29}$$

where

$$V_c = \sum_i \bar{V}(r_i) \tag{30}$$

and

$$v = V' - \sum_i \bar{V}(r_i) \tag{31}$$

The purpose of writing it in this manner is to highlight the spirit of the central field approximation where v and V_{so} are neglected. If we wish to go on to the next approximation, we have to assess the relative importance of v and V_{so}. The approximation $v \gg V_{so}$ leads to the so-called Russell-Saunders or L-S coupling scheme and is valid for light nuclei. The other extreme $V_{so} \gg v$ leads to j-j coupling.

L-S Coupling

Neglecting V_{so}, the Hamiltonian becomes

$$H = \sum T_i + \sum \bar{V}_i + v = H_0 + v \tag{32}$$

H_0, here, is then the Hamiltonian we use in the central field approximation. Since spin does not occur at all in Eq. (32), all the spin operators s_i^2, $(s_i)_z$, S^2 and S_z (where $\mathbf{S} = \sum_i \mathbf{s}_i$) commute with H and their eigenvalues are good quantum numbers.

So long as we consider only H_0, each electron moves *independently*, giving single particle wavefunctions. Hence, l_i^2, $(l_i)_z$, L^2 and L_z all commute with H_0. But the extra term v includes explicitly the interaction of electrons (although, a large part of the actual interaction has already been incorporated in the central field Hamiltonian H_0). Thus, the Hamiltonian H in Eq. (32) does not commute with each of the operators l_i any more. This is merely reiterating the obvious that for an interacting system, we cannot talk about angular momenta of parts of the system.

However, L^2 and L_z commute with the entire Hamiltonian. Moreover, the total angular momenta J^2 and J_z, where $\mathbf{J} = \mathbf{L} + \mathbf{S}$ commute with H.

Thus in this approximation, (i.e., neglecting V_{so}, giving the Russell-Saunders case), the state of an atom is specified by the quantum numbers L, M_L, S, M_S and M_J (we shall generally write M_J merely as M) corresponding to the eigenvalues of the various operators commuting with the Hamiltonian H. One must remember that although we refer to L as the eigenvalue of the total orbital angular momentum we really mean that $L(L+1)$ is the eigenvalue of L^2. Similar remarks apply for S and J.

As an example, consider Si_{14}. In the central field approximation, the single particle states are 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, etc. In accordance with the exclusion principle, the electron configuration is

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$$

with all but the 3*p* state filled to capacity. The two 3*p* electrons have $l_1 = 1$, $l_2 = 1$ and the total number of possible *states* with this configuration is

$$2(2l_1 + 1) \times 2(2l_2 + 1) = 36$$

But all these are not allowed by the exclusion principle. For example, $m_{l_1} = m_{l_2} = 1$ and $m_{s_1} = m_{s_2} = \frac{1}{2}$ is not allowed; these restrictions remove $2(2l + 1) = 6$ states out of contention. Of the remaining 30 only half are independent states due to the indistinguishability of electrons. For example, $m_{l_1} = m_{l_2} = 1$, $m_{s_1} = \frac{1}{2}$, $m_{s_2} = -\frac{1}{2}$ is the same state as the one with $m_{l_1} = m_{l_2} = 1$, $m_{s_1} = -\frac{1}{2}$, $m_{s_2} = \frac{1}{2}$.

In the central field approximation, all these states have the same energy. When we 'switch on' the correction term* v in the Hamiltonian H, this degeneracy is partially lifted. Assuming *L-S* coupling, we have the following possibilities

$$L = 0, 1, 2 \quad \text{and} \quad S = 0, 1$$

Imposing the constraint that the total wavefunction must be antisymmetric we have, for even L (space symmetric) only singlet states $S = 0$ (spin antisymmetric) and for odd L (space antisymmetric) only triplet states $S = 1$ (spin symmetric). We have $(2L + 1)(2S + 1)$ states so that we have

$L = 0,\ \ S = 0$ (1 state)
$L = 1,\ \ S = 1$ (9 states)
$L = 2,\ \ S = 0$ (5 states)

giving our 15 states. These states, however, no longer have the same energy.

16.8 Hund's Rules

Two empirical rules, first formulated by Hund, can be used to decide which ones have the lowest energy. The first rule is

For any given electron configuration, the energy level with the highest multiplicity (i.e. highest value of S) will have the lowest energy. For this S value, the level with the highest L value will be lowest in energy.

Thus, for S_i, we shall have $L = 1$, $S = 1$ and the state is designated by ^3P (notice that $L = 2$, $S = 1$ is forbidden). This still leaves a 9-fold degeneracy. Indeed, coupling L and S, we have the following possibilities: $J = 0, 1, 2$ so that the possible *terms* are ${}^3P_0$, ${}^3P_1$, and ${}^3P_2$ with $2J + 1 = 1$, 3 and 5 states in each of these terms. To settle which term has the lowest energy, we include the spin orbit interaction

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*This picturesque description is the theorist's license. Nature, of course, does not provide such 'switches' but it is a most convenient pretence to enable us to think in sequence. Particle physicists have, for years, been switching off weak, electromagnetic and other interactions.

$$V_{so} = \sum_i \xi(r_i)\, \mathbf{l}_i \cdot \mathbf{s}_i \tag{33}$$

According to perturbation theory, the energy shift, to first order, within a state of quantum numbers L, S due to V_{so} (regarded as a perturbation), is

$$\Delta E = \langle L, S, M_L, M_S \mid V_{so} \mid L, S, M_L, M_S \rangle \tag{34}$$

Now, it can be shown that this can be expressed as

$$\Delta E = \zeta(r, L, S) \langle \mathbf{L} \cdot \mathbf{S} \rangle \tag{35}$$

The expectation value $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ is readily calculated by writing

$$\mathbf{L} \cdot \mathbf{S} = \frac{(\mathbf{L} + \mathbf{S})^2 - L^2 - S^2}{2} \tag{36}$$

so that

$$\Delta E = \frac{J(J + 1) - L(L + 1) - S(S + 1)}{2} \zeta \tag{37}$$

This gives -2ζ, $-\zeta$ and ζ for the three terms ${}^3P_0$, ${}^3P_1$ and ${}^3P_2$ in our example. If ζ is positive, ${}^3P_0$ will have the lowest energy. Hund's second rule sanctifies this choice.

> *For normal multiplets, which arise from electron shells less than half full, the lowest energy is for $J = |L - S|$. For inverted multiplets, which arise from electron shells more than half full, the lowest energy is for $J = L + S$.*

16.9 Some Examples

We take as our first examples, the boron atom ($Z = 5$). The five electrons are distributed, one in each of the four electron states A to D [see Table 16.1] plus one in any one of the six electron states E to J. There are then six possible states of the boron atom as shown in Table 16.2*.

Let us now calculate the term symbol. Table 16.2 shows that the maximum values of M_L and M_S are 1 and $\frac{1}{2}$ respectively. Therefore $L = 1$, $S = \frac{1}{2}$ and the multiplicity $2S + 1 = 2$; i.e., the eigenstate is a doublet. The possible values of J are given by

$$L - S \leqslant J \leqslant L + S$$

Thus $J = \frac{1}{2}$ and $J = \frac{3}{2}$ There are then two eigenstates**

${}^2P_{1/2}$ and ${}^2P_{3/2}$

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*Tables 16.1 and 16.2 and the ensuing discussion have been adapted from Tralli and Pomilla (1969) (with the kind permission of the publishers).

**The notation for the term symbol is ${}^{2s+1}(L)_J$.

TABLE 16.1

Electron State	n_i	l_i	m_{l_i}	m_{s_i}
$A\ (i = 1)$	1	0	0	$\frac{1}{2}$
$B\ (i = 2)$	1	0	0	$-\frac{1}{2}$
$C\ (i = 3)$	2	0	0	$\frac{1}{2}$
$D\ (i = 4)$	2	0	0	$-\frac{1}{2}$
$E\ (i = 5)$	2	1	1	$\frac{1}{2}$
$F\ (i = 6)$	2	1	1	$-\frac{1}{2}$
$G\ (i = 7)$	2	1	0	$\frac{1}{2}$
$H\ (i = 8)$	2	1	0	$-\frac{1}{2}$
$I\ (i = 9)$	2	1	-1	$\frac{1}{2}$
$J\ (i = 10)$	2	1	-1	$-\frac{1}{2}$

TABLE 16.2

SIX POSSIBLE STATES OF THE BORON ATOM

State	$M_l = \sum_i m_{l_i}$	$M_s = \sum_i m_{s_i}$
$[A + B + C + D] + E$	1	$\frac{1}{2}$
$[A + B + C + D] + F$	1	$-\frac{1}{2}$
$[A + B + C + D] + G$	0	$\frac{1}{2}$
$[A + B + C + D] + H$	0	$-\frac{1}{2}$
$[A + B + C + D] + I$	-1	$\frac{1}{2}$
$[A + B + C + D] + J$	-1	$-\frac{1}{2}$

$L = 0, 1, 2, 3\ldots$ are denoted by $S, P, D, F\ldots$ respectively. The left superscript is the multiplicity. The right subscript J denotes the value of the total angular momentum quantum number.

According to Hund's second rule, the ground state is $^2P_{1/2}$. This detailed analysis may be avoided by ignoring closed shells altogether, leaving just the $2p$ electron. With $l = 1$, $s = \frac{1}{2}$, the same conclusion is reached; note that since $2p$ shell is less than half full, we expect a normal multiplet.

An another example, we consider oxygen: $1s^2\,2s^2\,2p^4$ and as before we consider only the $2p^4$ electrons. There are 6 possibilities as follows $(n = 2, l = 1)$.

State	m_l	m_s
a	1	$\frac{1}{2}$
b	1	$-\frac{1}{2}$
c	0	$\frac{1}{2}$
d	0	$-\frac{1}{2}$
e	-1	$\frac{1}{2}$
f	-1	$-\frac{1}{2}$

Since the four electrons can occupy precisely four of these states, it is simpler to ask which *two* states to leave out. There are 15 possibilities. It is easy to see, therefore, that the states *four p* electrons are precisely the same as for *two p* electrons, i.e., we can regard that there are two *holes* in the $2p$ shell. The possible states therefore are exactly as for carbon. However, we see that the $2p$ shell is more than half full and we expect *inverted* multiplets. Thus we expect the ground state of oxygen to be $^3P_2$ whereas the ground state of carbon will be $^3P_0$ in accordance with Hund's rules.

16.10 j-j Coupling

We now consider, briefly, the case when $V_{so} \gg v$. If we neglect v altogether, the Hamiltonian will commute with j_i, the total angular momentum for each electron, separately—this was not so for *L-S* coupling. Moreover, it can be easily shown that the Hamiltonian (neglecting v) will not commute with l_i and s_i separately. An atom, now, can be specified by the four quantum numbers L, S, J and M. Hence, we first couple each l_i and s_i to form j_i and then couple the various j_i to obtain the total angular momentum J. As an example, for a p^2 configuration in the same shell, j_1 and j_2 can be $\frac{3}{2}$ or $\frac{1}{2}$. One can have $J =$ 3, 2, 1 or 0; but for equivalent electrons, it can be shown that $J = 3$ is not possible*.

It is found that *L-S* coupling starts breaking down for heavier atoms but one seldom finds examples of pure *j-j* coupling. On the other hand, in nuclear structure, where spin orbit forces are large, *j-j* coupling is of greater range of validity.

PROBLEMS

PROBLEM 16.1

Show that the energy difference between two successive components of a multiplet (i.e., differing by unity in J values) is proportional to the *higher* J value of the pair. [Use Eqs. (35) and (37).] This is the famous Lande interval rule.

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*Equivalent electrons are those with the same values of n and l. The $J = 3$ case requires both electrons to occupy the same state and hence is forbidden by the exclusion principle; evidently for electrons with different n and l, this restriction does not apply.

PROBLEM 16.2

Obtain Eq. (13) by evaluating the integral given by Eq. (12).

PROBLEM 16.3

List the terms allowed by the exclusion principle for two electrons in d^2 configuration when they are (a) equivalent and (b) non-equivalent.

PROBLEM 16.4

Write down the terms for the cases: (a) $(ns)(n's)$, (b) $(ns)(n'd)$ and (c) $(np)(n'p)$. Consider both $n = n'$ and $n \neq n'$. Here n, n' are the principal quantum numbers of the two electrons.

PROBLEM 16.5

The $1s\ 2s$ state of helium lies about 20 eV above the ground state $1s^2$. (Actually, there are two terms, ${}^1s_0$ and ${}^3s_1$, the singlet having a somewhat higher energy. You may ignore this.)

Note that this corresponds to an energy about $-$ 59eV for the $1s\ 2s$. Show that this is about what one expects if we assume that the $1s$ electron moves in a nucleus of charge 2 and the $2s$ of charge 1.

Study this in relation to the comment that the self-consistent field for different electrons may not be the same and try to explain why the above naive picture, in the present case, works so well.

PROBLEM 16.6

Start with the potentials for the $1s$ and $2s$ electrons (for the $1s\ 2s$ state of helium) using the naive picture as above and then go through the procedure of Sec. 16.6 to calculate self-consistent potentials. The calculation is tedious but instructive and requires the use of a computer or at least a programmable calculator with a few hundred steps facility. Proceed as follows:

(a) Start with

$$u_{1s} = 25^{5/2} e^{-2r}\, r$$

and

$$u_{2s} = 2^{-3/2}(2-r)e^{-r/2}\, r$$

(where $R = u/r$) and calculate V_1 and V_2 from Eqs. (24) and (25).

(b) Now use these single particle potentials to work out the normalized wavefunctions u_{1s} and u_{2s} by integrating the corresponding Schrödinger equations.

(c) Strictly speaking, you will have to go back and do it all over again to calculate the next approximations for V_1 and V_2 from Eqs. (24) and (25). However, a fair result may be expected if you use the wavefunctions now from step (b) and calculate $\langle H \rangle$ from Eq. (16) using Eqs. (18), (19) and (21).

Do not forget that the term $\langle v_{12} \rangle$ must be added only once.

PROBLEM 16.7

Show that for a closed shell (as suggested in Sec. 16.10) $L = S = 0$.

SOLUTIONS

SOLUTION 16.1

Using Eq. (37), it is easily shown that

$$\Delta E\,(J, L, S) - \Delta E\,(J - 1, L, S) = J\zeta$$

SOLUTION 16.3

With $l_1 = l_2 = 2$; $s_1 = s_2 = \frac{1}{2}$; we have the following possible values for L, S and J

L	4	4	3	3	2	2	1	1	0	0
S	1	0	1	0	1	0	1	0	1	0
J	3, 4, 5	4	2, 3, 4	3	1, 2, 3	2	0, 1, 2	1	1	0

The corresponding terms are

$$^3G,\ ^1G;\ ^3F,\ ^1F;\ ^3D,\ ^1D;\ ^3P,\ ^1P;\ ^3S \text{ and } ^1S$$

By adding the values of $(2S + 1) \times (2L + 1)$ for each term *or* by working out $\Sigma(2J + 1)$ one can see that the total number of states is 100 which is, of course, just

$$2(2l_1 + 1) \times 2(2l_2 + 1)$$

All the terms are allowed for non-equivalent particles.

For equivalent particles (i.e., electrons with the same principal quantum number), the total wavefunction must be antisymmetric so that we can only have the combinations

$$S = 0, \text{ even } L$$

$$S = 1, \text{ odd } L$$

Thus only ^1G, ^3F, ^1D, ^3P and ^1S terms are allowed. Count the number of independent states.

SOLUTION 16.7

In a closed shell system all possible values of m_l and m_s are occupied; it means that for every positive value of m_l (and m_s) occupied there is an electron with an equally negative value of m_l (and m_s). Thus, for such a state

$$M = \Sigma m = \Sigma(m_l + m_s) = 0$$

where the sum runs over all electrons in the shell; M is the eigenvalue of J_z, the Z-component of the total angular momentum. Suppose the state in question is $|\psi_0\rangle$. Then, since the total angular momentum $\mathbf{J}$ and J^2 commute with the Hamiltonian, we can follow the same arguments as in Sec. 9.2 to show that $(J_x \pm iJ_y)|\psi_0\rangle$ must be a state with the same energy, same angular momentum j but with eigenvalue of J_z increased (or reduced, for the negative sign) by unity. Since, however, the closed shell state is non-degenerate, we demand that

$$(J_x \pm iJ_y)|\psi_0\rangle = 0$$

i.e., $|\psi_0\rangle$ is a state for which J_x, J_y and J_z all have zero eigenvalues. Hence we have $\mathbf{J} = 0$.

CHAPTER SEVENTEEN

Numerical Integration of Schrödinger's Equation

17.1 Introduction

In most problems in quantum mechanics, analytic solutions in terms of known functions cannot be found. We then have to resort to numerical methods. For complex atoms, the Hartree or Hartree-Fock methods require such techniques to a high degree of sophistication and there is no substitute for actual experience in handling such problems.* Nevertheless, it would be useful to learn some basic principles of such computation. We restrict ourselves to the solution of Schrödinger equation for a central field. The simple exercises treated here can all be carried out with a programmable calculator of the type available in many institutions.

17.2 General Principles

The radial equation for a particle moving in a central field can be written as

$$\left\{ \frac{d^2}{dr^2} + 2[E-V(r)] - \frac{l(l+1)}{r^2} \right\} u(r) = 0 \tag{1}$$

the complete wavefunction being

$$\psi(r) = \frac{u(r)}{r} Y_{l_m}(\theta, \varphi) \tag{2}$$

where Y_{l_m} are spherical harmonics. In writing down Eq. (1), we have used natural atomic units (see footnote on p. 375).

The differential equation may then be written as

$$u'' = F(r)u \tag{3}$$

where

$$F(r) = -2[E-V(r)] + \frac{l(l+1)}{r^2} \tag{4}$$

To solve this numerically, we divide the range of values of r (0 to ∞ in many cases) into fine intervals h, i.e.,

$$r = 0, h, 2h, \ldots$$

a particular value of r being denoted by r_j and the corresponding value of u (to be determined) by u_j. The essence of numerical calculus is to change continuous variations to finite intervals.

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*The reader is referred to the book by Hartree (1957) for an authoritative account of numerical methods used for atomic structure calculations. For a general account of numerical solutions of ordinary differential equations, we refer to Hartree (1958).

We introduce the so-called central difference

$$\delta u_j = u_{j+1/2} - u_{j-1/2} \tag{5}$$

Clearly, the second (central) difference is

$$\delta^2 u_j \equiv \delta(\delta u_j) = u_{j+1} - 2u_j + u_{j-i} \tag{6}$$

It is convenient to think of the symbols δ and δ^2 as operators which, acting on a particular u_j, produce the results given in Eqs. (5) and (6). They are just definitions and, hence, are exact relations. To relate it to a differential equation, we need relations between these (finite) differences and *derivatives* and such relations, of course, will be approximations. It can be shown* that

$$\delta^2 u_j = \left(1 + \frac{\delta^2}{12}\right) h^2 u_j'' + O(h^6) + \ldots \tag{7}$$

where $\delta^2(h^2 u_j'') = h^2 \delta^2 u_j''$ will have the same operational definition as in Eq. (6) and $O(h^6)$ represents terms of order h^6 and will be neglected. Substituting the expression for $\delta^2 u_j$ from Eq. (6) and for u_j'' from Eqs. (3) and (4) into Eq. (7), we obtain

$$\left(1 - \frac{h^2}{12} F_{j+1}\right) u_{j+1} = h^2 F_j u_j + 2\left(1 - \frac{h^2}{12} F_j\right) u_j - \left(1 - \frac{h^2}{12} F_{j-1}\right) u_{j-1} \tag{8}$$

where $F_j \equiv F(r_j)$, etc.

Equation (8) gives us a method to iterate values of u for increasing or decreasing values of r. In the former case (called *outward* integration), we start with known values of u_{j-1} and u_j (remember that F_{j-1}, F_j and F_{j+1} are all known values) and calculate u_{j+1}. We then repeat the procedure to calculate u_{j+2} from u_{j+1} and u_j and so on.

17.3 Matching the Outward and Inward Solutions

Hartree has given a simple procedure for matching the two solutions unless the value of E is the right one, the two will not match. For a particular value of E, we have

$$\left[\frac{d^2}{dr^2} - 2V(r) + 2E - \frac{l(l+1)}{r^2}\right] u = 0 \tag{9}$$

---

*This formula can be derived from the Taylor expansions

$$u_{j\pm 1} = u_j \pm h u_j' + \frac{h^2}{2} u_j'' \pm \frac{h^3}{6} u_j''' + \ldots$$

so that

$$\delta^2 u_j = h^2 u_j'' + \frac{h^4}{12} u_j^{\text{iv}} + \frac{h^6}{360} u_j^{\text{vi}} + \ldots.$$

Let $u + \Delta u$ be the solution for another choice $E + \Delta E$. Then

$$\left[\frac{d^2}{dr^2} - 2V(r) + 2(E + \Delta E) - \frac{l(l+1)}{r^2} \right] (u + \Delta u) = 0 \tag{10}$$

Neglecting the product $\Delta E \, \Delta u$, these two equations give

$$\left[\frac{d^2}{dr^2} - 2V(r) + 2E - \frac{l(l+1)}{r^2} \right] \Delta u = -2u \, \Delta E \tag{11}$$

Multiplying Eq. (9) by Δu, Eq. (11) by u and subtracting, we obtain

$$\frac{d^2u}{dr^2} \, \Delta u - u \, \frac{d^2(\Delta u)}{dr^2} = 2u^2 \Delta E$$

The operations d^2/dr^2 and Δ are interchangeable so that we can write

$$\frac{d}{dr} \left[u' \, \Delta u - u \Delta u' \right] = 2u^2 \, \Delta E$$

where $u' = du/dr$. Integrating, we get

$$\left[u' \Delta u - u \Delta u' \right]_{r_1}^{r_2} = 2\Delta E \int_{r_1}^{r_2} u^2 dr \tag{12}$$

Writing the left-hand side of Eq. (12) as $-u^2 \Delta \, (u'/u)$ we have

$$\left[u^2 \, \Delta \left(\frac{u'}{u} \right) \right]_{r_1}^{r_2} = -2\Delta E \int_{r_1}^{r_2} u^2 dr \tag{13}$$

For the outward integration, we set $r_1 = 0$, $r_2 = r_0$ and $u(0) = 0$, so that

$$\left[u^2 \, \Delta \left(\frac{u'}{u} \right) \right]_{r_0} = -2\Delta E \int_0^{r_0} u^2 \, dr \tag{14}$$

Similarly, for the inward integration we set $r_1 = r_0$, $r_2 = \infty$ and $u(\infty) = 0$, so that

$$-\left[u^2 \, \Delta \left(\frac{u'}{u} \right) \right]_{r_0} = -2\Delta E \int_{r_0}^{\infty} u^2 dr \tag{15}$$

Thus (writing $\mathcal{E} = -E > 0$)

$$\left[\Delta \left(\frac{u'}{u} \right)_{r_0} \right]_{\text{out}} = \frac{2\Delta \mathcal{E}}{[u^2(r_0)]_{\text{out}}} \int_0^{r_0} u_{\text{out}}^2 \, dr \tag{16}$$

and

$$\left[\Delta \left(\frac{u'}{u} \right)_{r_0} \right]_{\text{in}} = \frac{-2\Delta \mathcal{E}}{[u^2(r_0)]_{\text{in}}} \int_{r_0}^{\infty} u_{\text{in}}^2 \, dr \tag{17}$$

and the values of u'/u should be the same for the correct values of $\mathcal{E}$. Suppose, for example, $(u'/u)_{\text{out}}$ is larger than $(u'/u)_{\text{in}}$. We clearly have to *reduce* $\mathcal{E}$, i.e., $\Delta\mathcal{E} < 0$. Indeed, from Eqs. (16) and (17) we obtain

$$\left[\frac{\int_0^{r_0} u_{\text{out}}^2 dr}{u_{\text{out}}^2(r_0)} + \frac{\int_{r_0}^{\infty} u_{\text{in}}^2\, dr}{u_{\text{in}}^2(r_0)}\right] 2\Delta\mathcal{E} = -\left[\left(\frac{u'}{u}\right)_{\text{out}} - \left(\frac{u'}{u}\right)_{\text{in}}\right]_{r_0} \tag{18}$$

a relation easily obtained by setting

$$\left(\frac{u'}{u}\right)_{\text{out}} + \Delta\left(\frac{u'}{u}\right)_{\text{out}} = \left(\frac{u'}{u}\right)_{\text{in}} + \Delta\left(\frac{u'}{u}\right)_{\text{in}}$$

Equation (18) is used to estimate $\Delta\mathcal{E}$ and the revised estimate $\mathcal{E}$ may be used to repeat the whole procedure, if necessary.

The matched solution may then be normalized to give

$$\int_0^{\infty} u^2 dr = 1$$

17.4 The Hydrogen Atom as an Example

We shall illustrate the method by calculating the ground state energy of the hydrogen atom. Here $V = -1/r$ and $F = -2(E + 1/r)$. Our procedure is to integrate *outwards* from $r = 0$ to $r = 2$ in steps of $h = 0.1$ and to integrate inwards from $r = 10$ to $r = 2$ in steps of $h = 0.5$ and see how to 'match' solutions at $r = 2$. We hope that $u(r = 10)$ is sufficiently small. To start the outward integration, we need a few values of u for small r. We write

$$u(r) = \sum_{n=1}^{\infty} a_n r^n \tag{19}$$

since we know that for small r, the leading term in u behaves like r^{l+1}. Substituting Eq. (19) into Eq. (3) with $F(r) = -2(E + 1/r)$ and comparing coefficients of r, we obtain

$$\begin{aligned} a_2 &= -a_1 \\ 6a_3 &= -2Ea_1 - 2a_2 \\ 12a_4 &= -2Ea_2 - 2a_3 \end{aligned} \tag{20}$$

Choosing $a_1 = 1$, we obtain

$$u = r - r^2 + \frac{(1-E)r^3}{3} + \frac{(4E-1)r^4}{18} + \cdots \tag{21}$$

which can be used to obtain the first few values of u, say up to $r = 0.4$.

To start the inward integration, we note that for large r, $F(r)$ is very nearly constant, so that

$$u(r) \approx A \exp(-\sqrt{F(r)}\, r) \tag{22}$$

Fixing, arbitrarily, the value of $u(R)$ at $r = R$, we have

$$A = u(R) \exp(R\sqrt{F})$$

so that

$$u(R - h) = u(R) \exp(h\sqrt{F})$$

We can now proceed to use the iteration formula, Eq. (8) with

$$u_j = u(R - h) \text{ and } u_{j+1} = u(R)$$

In practice, it is not really necessary to use a large value of R; typically, we have tried $R = 5$, $h = 0.1$ (same interval as for the outward integration) and started with a guess of $\mathcal{E} = 1.0$. Successive iterations gave $\mathcal{E} = 0.330$, 0.426, 0.484 and 0.498. (The exact value is $\mathcal{E} = 0.5$). We have plotted the calculations for $\mathcal{E} = 1$ and for $\mathcal{E} = 0.33$ just to show what happens for incorrect values (see Fig. 17.1). We recommend that students try these calculations with a calculator to get a feel for numerical methods.

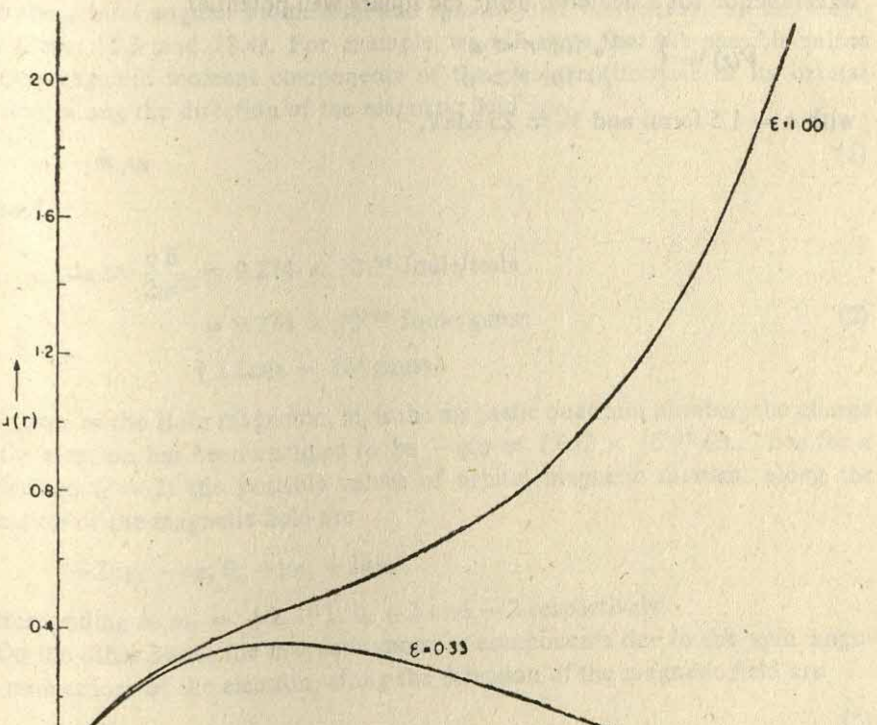

Fig. 17.1 The variation of $u(r)$ with r for $\mathcal{E} = 1.00$ and $\mathcal{E} = 0.33$.

PROBLEMS

PROBLEM 17.1

For large r, $V(r) \to 0$ and the radial equation (for $l = 0$) may be written as

$$u'' = -2 \mid E \mid u(r)$$

This means that if $u(r) > 0$ (< 0) the curvature is negative (positive). Perform the outward numerical integration for hydrogen atom ground state for $\mid E \mid = 1$ and $\mid E \mid = 0.3$ and plot $u(r)$ up to $r \approx 5$. For $\mid E \mid = 1$, you will find $u(r) \to -\infty$ and for $\mid E \mid = 0.3$, $u(r) \to +\infty$. Study, particularly, the shape of the curves as they diverge from the r axis.

PROBLEM 17.2

Consider the one-dimensional potential well $V = -V_0$ for $\mid x \mid < a$ and $V = 0$ for $\mid x \mid > a$. How do you expect $\psi(x)$ to behave for large x when (i) ψ' has too small a value at a and (ii) ψ' has too large a value at a?

PROBLEM 17.3

Perform the numerical integration to obtain the ground state energy and wavefunction for a deuteron using the square well potential

$$V(r) = \begin{cases} -V_0 & \text{for } r < a \\ 0 & \text{for } r > a \end{cases}$$

with $a = 1.5$ fermi and $V_0 \approx 25$ MeV.

CHAPTER EIGHTEEN

Effects of Magnetic Field

18.1 Introduction

Studies on the interaction of magnetic field with particles are of immense importance in many diverse areas. For example, in spectroscopy, the splitting of spectral lines in a magnetic field (which leads to Zeeman and Paschen-Back effects, see Problems 18.1 to 18.4) is a subject of considerable importance (see, e.g., White, 1934). In solid state physics, the calculation of diamagnetic and paramagnetic susceptibilities (see Problem 18.13) and the experiments on electron spin resonance and nuclear magnetic resonance (see Sec. 18.6 and Problems 18.8 to 18.10) have immense practical importance (see, e.g., Seitz, 1940; Slichter, 1963; Van Vleck, 1932; Wagner, 1972).

In this chapter we will discuss the interaction of magnetic field with particles. We will first develop the Hamiltonian of a charged particle in an electromagnetic field (Sec. 18.2) and will then discuss the interaction of the magnetic field with the orbital angular momentum and spin angular momentum of the electron (Secs. 18.3 and 18.4). For example, we will show that the possible values of the magnetic moment components of the electron (because of its orbital motion) along the direction of the magnetic field are

$$-m_l\mu_B \tag{1}$$

where*

$$\begin{aligned}\mu_B \equiv \frac{q\hbar}{2m} &= 9.274 \times 10^{-24}\ \text{Joule/tesla}\\ &= 9.274 \times 10^{-28}\ \text{Joule/gauss}\\ &(\ 1\ \text{tesla} = 10^4\ \text{gauss})\end{aligned} \tag{2}$$

is known as the Bohr magneton, m_l is the magnetic quantum number; the charge of the electron has been assumed to be $-q(q \simeq 1.602 \times 10^{-19}\ \text{C})$. Thus for a d-electron ($l = 2$) the possible values of orbital magnetic moment along the direction of the magnetic field are

$$-2\mu_B,\ -\mu_B,\ 0,\ +\mu_B,\ +2\mu_B$$

corresponding to $m_l = +2, +1, 0, -1$ and -2 respectively.

On the other hand, the magnetic moment components due to the spin angular momentum of the electron, along the direction of the magnetic field are

$$\pm\tfrac{1}{2}\, g\mu_B \simeq \pm\mu_B \tag{3}$$

---

*In Chapter 5, the magnetic quantum number is denoted by m, here it is denoted by m_l to avoid confusion with the electron mass.

where g is known as the gyromagnetic ratio ($\simeq 2.0023$). The corresponding proton magnetic moment is

$$\pm \tfrac{1}{2} g_p \mu_p \tag{4}$$

where $g_p \simeq 5.56$, $\mu_p = q\hbar/2M = 5.051 \times 10^{-31}$ Joule/gauss.

In Sec. 18.5 we will discuss the spin-orbit interaction. In Sec. 18.6 we will discuss the basic principle of magnetic resonance experiments.

18.2 The Hamiltonian

We first define the vector and scalar potentials. From the Maxwell equation

$$\nabla \cdot \mathbf{B} = 0 \tag{5}$$

it immediately follows that B can be expressed as the curl of a vector

$$\mathbf{B} = \nabla \times \mathbf{A} \tag{6}$$

where A is known as the vector potential. Further, if we substitute this in the equation

$$\nabla \times \mathcal{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{7}$$

we would get

$$\nabla \times \left(\mathcal{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = 0 \tag{8}$$

Thus we may set

$$\mathcal{E} = -\frac{\partial \mathbf{A}}{\partial t} - \nabla\phi \tag{9}$$

where ϕ is known as the scalar potential.

We next consider the motion of a charged particle (of charge Q) in an electromagnetic field. The force acting on the charged particle is given by

$$\mathbf{F} = Q\,[\,\mathcal{E} + \mathbf{v} \times \mathbf{B}\,] \tag{10}$$

or

$$m\frac{d\mathbf{v}}{dt} = \mathbf{F} = Q\left[-\frac{\partial \mathbf{A}}{dt} - \nabla\phi + \mathbf{v} \times (\nabla \times \mathbf{A}) \right]$$

Now

$$(\mathbf{v} \times \nabla \times \mathbf{A})_x = v_y \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) - v_z \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right)$$

$$= \frac{\partial}{\partial x}(\mathbf{v} \cdot \mathbf{A}) - \frac{dA_x}{dt} + \frac{\partial A_x}{dt}$$

where use has been made of the relation

$$\frac{dA_x}{dt} = \frac{\partial A_x}{dt} + \left(v_x \frac{\partial A_x}{\partial x} + v_y \frac{\partial A_x}{\partial y} + v_z \frac{\partial A_x}{\partial z} \right)$$

Thus

$$\frac{d}{dt}[m\mathbf{v} + Q\mathbf{A}] = \nabla[-Q\phi + Q(\mathbf{v}\cdot\mathbf{A})] \tag{11}$$

Equation (11) can be written in the form

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) = \frac{\partial L}{\partial x} \tag{12}$$

(and similar equations with x replaced by y and z) where

$$L = \tfrac{1}{2}m\mathbf{v}\cdot\mathbf{v} - Q\phi + Q\,\mathbf{A}\cdot\mathbf{v} \tag{13}$$

Equation (12) is the Lagrangian equation of motion (see, e.g., Goldstein, 1950) and L denotes the Lagrangian. The conjugate momenta are given by

$$p_x = \frac{\partial L}{\partial \dot{x}} = m\mathrm{v}_x + Q\mathrm{A}_x$$

or

$$\mathbf{p} = m\mathbf{v} + Q\mathbf{A} \tag{14}$$

The Hamiltonian is given by

$$\begin{aligned} H &= \mathbf{p}\cdot\mathbf{v} - L \\ &= \mathbf{p}\cdot\left[\frac{1}{m}\left(p - QA\right)\right] - \frac{1}{2}m\left[\frac{1}{m}\left(\mathbf{p} - Q\,\mathbf{A}\right)\right]^2 \\ &\qquad + Q\phi - Q\mathbf{A}\cdot\frac{1}{m}(\mathbf{p} - Q\mathbf{A}) \\ &= \frac{1}{2m}[\mathbf{p} - Q\mathbf{A}]^2 + Q\phi \end{aligned} \tag{15}$$

Equation (15) represents the Hamiltonian describing the non-relativistic motion of a charged particle in an electromagnetic field.

In order to write the Schrödinger equation, we replace the operator $\mathbf{p}$ by $-i\hbar\nabla$ to obtain

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \tag{16}$$

where $$H = \frac{1}{2m}[-i\hbar\nabla - Q\mathbf{A}]^2 + Q\phi \tag{17}$$

18.3 The Schrödinger Equation Corresponding to a Static Electromagnetic Field

For a static electromagnetic field the wavefunction can be written in the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\, e^{-iEt/\hbar} \tag{18}$$

where $\psi(\mathbf{r})$ satisfies the equation

$$\frac{1}{2m}\left[-i\hbar\nabla - Q\mathbf{A}\right]^2\psi + Q\phi\psi = E\psi$$

or

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \frac{iQ\hbar}{2m}\left[\nabla\cdot(\mathbf{A}\psi) + \mathbf{A}\cdot\nabla\psi\right] + \left[\frac{Q^2}{2m}A^2 + Q\phi\right]\psi = E\psi \qquad (19)$$

Now, in the Coulomb gauge*, $\nabla\cdot\mathbf{A} = 0$ and we have

$$\nabla\cdot(\mathbf{A}\,\psi) = (\nabla\cdot\mathbf{A})\,\psi + \mathbf{A}\cdot\nabla\psi = \mathbf{A}\cdot\nabla\psi$$

which gives

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \frac{iQ\hbar}{m}\mathbf{A}\cdot\nabla\psi + \left[\frac{Q^2}{2m}A^2 + Q\phi\right]\psi = E\,\psi \qquad (20)$$

Further, for a uniform magnetic field, we can always write**

$$\mathbf{A} = \tfrac{1}{2}(\mathbf{B}\times\mathbf{r}) \qquad (21)$$

Thus the second term in Eq. (20) becomes

$$\begin{aligned}\frac{iQ\hbar}{m}\mathbf{A}\cdot\nabla\psi &= \frac{iQ\hbar}{2m}(\mathbf{B}\times\mathbf{r})\cdot\nabla\psi\\ &= -\frac{Q}{2m}\mathbf{B}\cdot[\mathbf{r}\times(-i\hbar\nabla)]\,\psi\\ &= -\frac{Q}{2m}\mathbf{B}\cdot(\mathbf{r}\times\mathbf{p})\,\psi = -\frac{Q}{2m}(\mathbf{B}\cdot\mathbf{L})\,\psi\\ &= -\boldsymbol{\mu}_o\cdot\mathbf{B}\,\psi\end{aligned} \qquad (22)$$

where $\mathbf{L} = \mathbf{r}\times\mathbf{p}$ represents the orbital angular momentum and

$$\boldsymbol{\mu}_o = \frac{Q}{2m}\mathbf{L} \qquad (23)$$

---

*From Eq. (6), we see that $\mathbf{B}$ is left unchanged if we add gradient of a scalar to $\mathbf{A}$

$$\mathbf{A}\rightarrow\mathbf{A}' + \nabla\chi.$$

We may choose χ such that $\nabla\cdot\mathbf{A} = 0$; this is known as the Coulomb gauge [for further details see Jackson (1961)].

** $\nabla\times\mathbf{A} = \tfrac{1}{2}\nabla\times(\mathbf{B}\times\mathbf{r}) = \tfrac{1}{2}[(\nabla\cdot\mathbf{r})\,\mathbf{B} - (\mathbf{B}\cdot\nabla)\,\mathbf{r}] = \tfrac{1}{2}[3\mathbf{B} - \mathbf{B}] = \mathbf{B}$

Also notice that

$$\nabla\cdot\mathbf{A} = \tfrac{1}{2}\nabla\cdot(\mathbf{B}\times\mathbf{r}) = \tfrac{1}{2}[\mathbf{r}\cdot(\nabla\times\mathbf{B}) - \mathbf{B}\cdot(\nabla\times\mathbf{r})] = 0$$

because the field is uniform.

can be interpreted as the magnetic moment associated with the orbital motion of the charged particle* (the subscript o signifies that the magnetic moment refers to the orbital motion). This follows from the fact that the interaction energy of a magnet (with magnetic moment $\boldsymbol{\mu}_o$) in a uniform magnetic field is given by**

$$U = -\boldsymbol{\mu}_o \cdot \mathbf{B} \tag{24}$$

Equation (20) therefore assumes the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \left(\frac{Q}{2m}\mathbf{L}\cdot\mathbf{B}\right)\psi + \frac{Q^2}{8m}(\mathbf{B}\times\mathbf{r})^2\psi + Q\phi\psi = E\psi \tag{25}$$

The second term has just been physically interpreted as the magnetic interaction energy associated with the circulatory motion of the charged particle; the third term can also be interpreted in terms of a potential energy function (see, e.g., Powell and Crasemann, 1961, Sec. 10.6), however, the considerations are rather involved. Further, since the term is proportional to the square of the magnetic field, it makes a negligible contribution unless the fields are extremely high.

18.4 The Interaction of the Magnetic Field with the Spin Angular Momentum of the Electron

In Sec. 9.2 we had discussed that electron is endowed with an intrinsic spin angular momentum given by

$$\mathbf{s} = \tfrac{1}{2}\hbar\boldsymbol{\sigma} \tag{26}$$

where σ_x, σ_y and σ_z are the Pauli matrices. Further, the magnetic moment associated with the spin angular momentum of a particle of charge Q has the form [cf. Eq. (23)]

$$\boldsymbol{\mu} = g\,\frac{Q}{2m}\,\mathbf{s} \tag{27}$$

---

*Equation (23) can be physically understood by noting that a charge Q rotating (in the anticlockwise direction) in a circle of radius r with speed v constitutes a current $I = Qv/2\pi r$ and therefore the magnetic moment associated with this motion is given by (see, e.g., Mendiratta and Sawhney, 1976, p. 152)

$$\boldsymbol{\mu} = \frac{Qv}{2\pi r}\,\mathbf{A} = \frac{Qv}{2\pi r}\,\pi r^2\,\hat{\mathbf{z}} = \frac{Q}{2m}\cdot\mathbf{r}\times\mathbf{p} = \frac{Q}{2m}\,\mathbf{L}$$

where we have assumed the circular motion to be in the $x-y$ plane and the area vector $\mathbf{A}$ points in the positive z-direction for anticlockwise motion.

**See, e.g., Panofsky and Phillips, 1962, p. 19.

where g is known as the gyromagnetic ratio. For the electron* $g \simeq 2$ and $Q = -q$, for the proton $g = 5.56$, $Q = +q$ and m has to be replaced by the proton mass.

Thus the total magnetic moment of the electron is given by

$$\mu_{\text{total}} = -\frac{q}{2m}\left[\mathbf{L} + g\mathbf{s}\right] \simeq -\frac{q}{2m}\left[\mathbf{L} + 2\mathbf{s}\right] \tag{28}$$

18.5 The Spin-Orbit Interaction

In order to physically understand the spin-orbit interaction we note that an observer who is at rest with the electron sees the nucleus moving around him; the circulating nucleus constitutes a current and produces a magnetic field at the electron given by

$$\mathbf{B} = \frac{1}{c^2}\,\mathbf{v} \times \mathbf{E}$$

where $\mathbf{E}$ represents the electric field produced at the electron by the nucleus and $\mathbf{v}$ the velocity of the electron. For a central potential

$$-q\mathbf{E} = -\nabla V = -\frac{1}{r}\frac{dV}{dr}\,\mathbf{r} \tag{29}$$

Thus

$$\mathbf{B} = \frac{1}{qc^2}\,\frac{1}{r}\,\frac{dV}{dr}\,\frac{1}{m}\,\mathbf{L} \tag{30}$$

where $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ represents the angular momentum. The interaction energy with the magnetic moment of the electron is given by

$$\begin{aligned} H_{s\text{-}o} &= -\tfrac{1}{2}\,\boldsymbol{\mu}\cdot\mathbf{B} = -\frac{1}{2}\left[-g\,\frac{q}{2m}\,\mathbf{s}\right]\cdot\left[\frac{1}{qc^2}\,\frac{1}{r}\,\frac{dV}{dr}\,\frac{1}{m}\,L\right] \\ &= \frac{g}{4m^2c^2}\,\frac{1}{r}\,\frac{dV}{dr}\,\mathbf{L}\cdot\mathbf{s} \end{aligned} \tag{31}$$

where the additional factor of $\frac{1}{2}$ is known as the Thomas precession factor and it comes from a proper relativistic treatment (Thomas, 1926). The subscript *s-o* on H implies spin-orbit interaction. For the Coulomb potential

$$V(r) = \frac{-Zq^2}{4\pi\epsilon_0 r} = -\frac{Ze^2}{r}$$

---

*The relativistic theory of Dirac predicts $g = 2$ (see Chapter 23); however, relativistic quantum electrodynamics shows that

$$g = 2 + \alpha/2\pi + O(\alpha^2)$$

where $\alpha\ (= q^2/4\pi\epsilon_0\hbar_c\, C \simeq 1/137)$ is the fine structure constant. For the proton, g is very different from 2 and hence it is not really a pure Dirac particle. It may be mentioned that neutral particles like neutrons, Λ, Σ^0 (which have spin $\frac{1}{2}$) have finite magnetic moments; e.g. for the neutron $\mu = -3.83\,(q/2m_n)\,\mathbf{s}$. Physically this arises from internal current distributions.

and

$$H_{s\cdot o} = \frac{gZ\hbar\alpha}{4m^2c}\,\frac{1}{r^3}\,\mathbf{L}\cdot\mathbf{s} \tag{32}$$

It may be mentioned that the spin-orbit interaction comes out automatically through a proper relativistic treatment (see Sec. 23.8).

18.6 Magnetic Resonance Experiments

In Problem 18.8 we will consider an electron in a uniform magnetic field (of magnitude B_0) in the z-direction. The energy eigenvalues will be

$$+\tfrac{1}{2}\,\hbar\omega_0 \quad\text{and}\quad -\tfrac{1}{2}\,\hbar\omega_0, \quad \left(\omega_0 = \frac{gqB_0}{2m} \simeq \frac{qB_0}{m}\right)$$

The corresponding eigenkets will be the spin up and spin down states respectively (denoted by $|\hat{\mathbf{z}}\uparrow\rangle$ and $|\hat{\mathbf{z}}\downarrow\rangle$). In addition to the uniform field in the z-direction, if we apply a rotating r.f. (radio frequency) field in the $x-y$ plane given by

$$B_x = B_1\cos\omega t,\;\; B_y = B_1\sin\omega t,\;\; B_z = 0 \tag{33}$$

then this r.f. field causes transitions between the two spin states. Indeed in Problem 18.10 we will show that if at $t = 0$, the system is in the $|\hat{\mathbf{z}}\uparrow\rangle$ state, then the spin-flip probability is given by

$$P_{\text{spin-flip}} = \frac{\omega_1^2}{\left(\dfrac{\omega-\omega_0}{2}\right)^2 + \omega_1^2}\,\sin^2\Gamma t \tag{34}$$

where

$$\Gamma = \left[\left(\frac{\omega-\omega_0}{2}\right)^2 + \omega_1^2\right]^{\frac{1}{2}} \tag{35}$$

and

$$\omega_1 = \frac{gqB_1}{2m} \simeq \frac{qB_1}{m} \tag{36}$$

The condition $\omega = \omega_0$ is known as the resonance condition and the spin flips for certainty at $t = \pi/2\Gamma, 3\pi/2\Gamma, \ldots$. The resonance condition is achieved either by varying the frequency of the r.f. field (ω) or by varying the strength of the d.c. magnetic field B_0 (and hence ω_0). Notice that the resonance becomes sharper as the value of B_1 is made smaller—see Fig. 18.1.

Now, at a particular temperature, the number of particles in the $|\hat{\mathbf{z}}\uparrow\rangle$ state (which has higher energy) will be less in comparison to the number of particles in the $|\hat{\mathbf{z}}\downarrow\rangle$ state. Further, when a transition occurs from the $|\hat{\mathbf{z}}\downarrow\rangle$ state

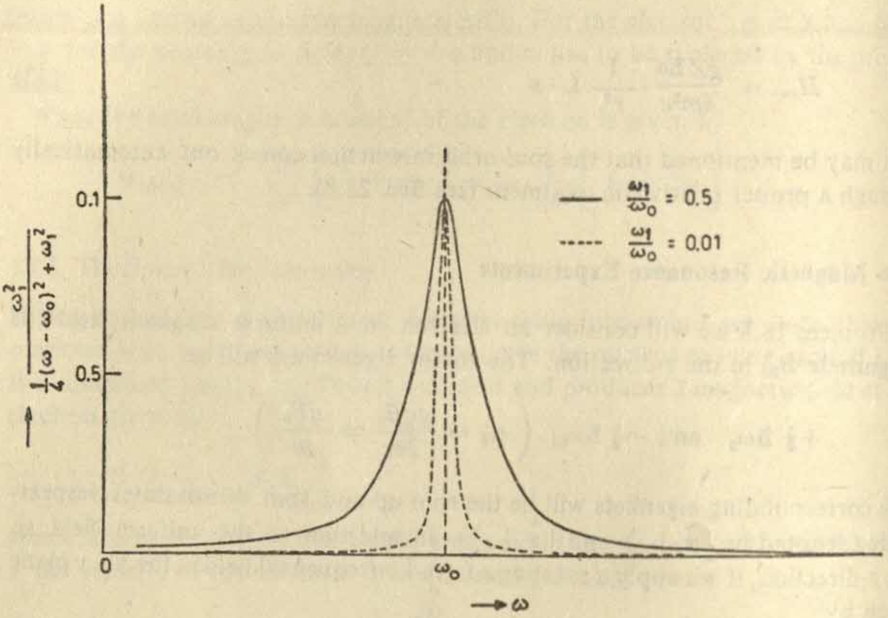

Fig. 18.1 The resonance condition corresponds to $\omega = \omega_0$, where the spin flips for certainty. The solid and the dashed curves correspond to ω_1/ω_0 ($= B_1/B_0$) $= 0.5$. and 0.01 respectirely. The resonance becomes sharper for smaller values of B.

to the $|\hat{z}\uparrow\rangle$ state, energy is supplied by the r.f. field. At resonance, the probability of spin flip will be maximum and hence the power supplied by the r.f. field will be maximum. This is the basic principle behind the electron spin resonance (ESR) and nuclear magnetic resonance (NMR) experiments which primarily involve obtaining the resonance condition $\omega = \omega_0$. This condition can be used either to accurately measure static magnetic fields (assuming the value of the electron magnetic moment or the proton magnetic moment) or to determine the magnetic moment of the atomic system.

PROBLEMS

PROBLEM 18.1

For a hydrogen atom placed in a weak uniform magnetic field (in the z-direction) the Hamiltonian will be the form

$$H = H_0 + H' \tag{37}$$

where

$$H_0 = \frac{p^2}{2m} + V(r) \tag{38}$$

and

$$H' = \frac{q}{2m} \mathbf{B} \cdot \mathbf{L} = \frac{\mu_B B}{\hbar} L_z \tag{39}$$

represents the interaction with the magnetic field (see Eq. 24); we have neglected the effects due to spin angular momentum of the electron (see Problem 18.2). Treat H' as perturbation and show that s states ($l = 0$) are not split whereas the p-states ($l = 1$) are split into three states separated by the energy interval $\mu_B B$. This is known as the normal Zeeman effect.

[*Note*: In this particular problem the perturbation calculation gives the exact results.]

PROBLEM 18.2

In continuation with the previous problem, if we take into account the effects due to spin angular momentum of the electron, the Hamiltonian will be of the form

$$H = H_0 + H' + H'' \tag{40}$$

where H_0 is given by Eq. (38), H' represents the spin-orbit interaction (see Eq. 32)

$$H' = f(r)\, \mathbf{L} \cdot \mathbf{s},\ f(r) = \frac{gZ\hbar\alpha}{4m^2c} \frac{1}{r^3} \tag{41}$$

and

$$H'' = \frac{qB}{2m} \left[L_z + gs_z \right] = \frac{\mu_B B}{\hbar} \left[L_z + gs_z \right] \tag{42}$$

represents the interaction with the magnetic field [see Eq. (28)]. Assume that the effect of H'' to be small in comparison to the effect of H', use the wavefunctions corresponding to H' as the perturbation [see Problem 11.12, Eq. (112) of Chapter 11 and Problem 9.12] to calculate the effect of H''. This is known as the weak-field anamolous Zeeman effect, or just Zeeman effect.

PROBLEM 18.3

Consider again the hydrogen like atom in a magnetic field **B**. Assume the magnetic field to be so strong that the effect of the spin-orbit interaction to be small compared to the effect of the magnetic field. Using the eigenfunctions of $H_0 + H''$, calculate the perturbation due to spin-orbit interaction. This is known as the Paschen-Back effect.

PROBLEM 18.4

The previous two problems correspond to weak magnetic fields and strong magnetic fields respectively. For the intermediate field case, $H' + H''$ has to be treated as perturbation to H_0. Use degenerate state perturbation theory to calulate the effect of $H' + H''$.

PROBLEM 18.5

In the following problem we will consider the effect of the proton magnetic moment and hence the hyperfine structure. However, before we do so, we note that the electron and proton can have their spins up or down; thus there are four possible spin states

$$|e\uparrow p\uparrow\rangle,\ |e\uparrow p\downarrow\rangle,\ |e\downarrow p\uparrow\rangle \text{ and } |e\downarrow p\downarrow\rangle \tag{43}$$

where the state $|e\uparrow p\downarrow\rangle$ corresponds to electron spin up and proton spin down, etc. Show that the operator

$$P = \tfrac{1}{2}[1 + \sigma_e \cdot \sigma_p] \tag{44}$$

is the spin exchange operator, i.e., when P operates on any of the four states, the spin directions are exchanged. Thus

$$P|e\uparrow p\downarrow\rangle = |e\downarrow p\uparrow\rangle, \text{etc.}$$

In Eq. (44) σ_e and σ_p represent the Pauli spin matrices for electron and proton respectively; further σ_e acts only on the electron spin and σ_p acts only on the proton spin.

PROBLEM 18.6

The magnetic field due to the proton magnetic moment interacts with the magnetic moment of the electron to give rise to the following interaction energy for s states [see Eq. (23-193) of Baym, 1969].

$$H' \simeq \frac{\epsilon}{n^3}\,\sigma_e \cdot \sigma_p \tag{45}$$

where

$$\epsilon = \frac{8}{3a_0^3}\,\mu_p\,\mu_B = \frac{8}{3a_0^3}\left(g_p\,\frac{q\hbar}{4M_p}\right)\left(g_e\,\frac{q\hbar}{4m}\right) \tag{46}$$

g_p ($\simeq 5.56$) and g_e ($\simeq 2.0$) represent the gyromagnetic ratios of proton and electron respectively; M_p represents the proton mass. Show for the ground state ($n = 1$) H' leads to the (hyperfine) splitting of 4ϵ which leads to the 21 cm line.

PROBLEM 18.7

In continuation of the previous problem, if we put the hydrogen atom in a magnetic field, the interaction energy (for $n = 1$) is

$$H' = \mu_B\,\sigma_{ez}B - \mu_p\sigma_{pz}B + \epsilon\,\sigma_e \cdot \sigma_p \tag{47}$$

Calculate the corresponding splitting and the spin wavefunctions.

PROBLEM 18.8

Consider an electron in a uniform magnetic field which is assumed to be in the z-direction. Neglect all orbital motion and write down the Hamiltonian representing the interaction of the magnetic field with the magnetic moment of the electron. Solve the time dependent Schrödinger equation and assuming $|\Psi(0)\rangle = |\hat{x}\uparrow\rangle$ calculate $|\Psi(t)\rangle$ and hence the time dependence of $\langle s_x\rangle, \langle s_y\rangle$ and $\langle s_z\rangle$. Show the Larmor precession.

PROBLEM 18.9

In Problem 18.8, instead of solving the time dependent Schrödinger equation, solve the Heisenberg equation of motion (see Sec. 8.12) for s_x, s_y and s_z. For

$$|\Psi(0)\rangle = \cos\varphi/2\,|\hat{z}\uparrow\rangle + \sin\varphi/2\,|\hat{z}\downarrow\rangle \tag{48}$$

calculate $\langle s_x(t)\rangle$, $\langle s_y(t)\rangle$ and $\langle s_z(t)\rangle$ and interpret the results physically.

PROBLEM 18.10

In continuation of Problem 18.8, assume that in addition to the uniform magnetic field in the z-direction, there is a rotating r.f. field given by Eq. (33). Obtain an exact solution of the time-dependent Schrödinger equation using a method similar to that used in Sec. 20.2. Assuming that at $t = 0$ the spin state is given by $|\hat{z}\uparrow\rangle$, calculate the probability for spin-flip at time t. The importance of such a result is discussed in Sec. 18.6.

PROBLEM 18.11

For a uniform magnetic field in the z-direction, we may assume

$$A_x = 0,\ A_y = xB,\ A_z = 0 \tag{49}$$

(Notice that $\nabla \times \mathbf{A} = B\hat{\mathbf{z}}$ and $\nabla \cdot \mathbf{A} = 0$). Write down the corresponding Schrödinger equation for an electron and obtain an exact solution of the same*. How would the eigenvalues get modified if the magnetic moment associated with the spin angular momentum is also taken into account.

PROBLEM 18.12

In the above problem, if we assume A to be given by Eq. (21), show that the same values for the energy eigenvalues are obtained; the wavefunctions however differ by an unimportant phase factor.

PROBLEM 18.13

In continuation with Problem 18.11, consider an electron in a spherically symmetric potential experiencing a uniform magnetic field in the z-direction for which A may be assumed to be of the form

$$A_x = -\tfrac{1}{2}\,yB,\ A_y = \tfrac{1}{2}\,xB,\ A_z = 0 \tag{50}$$

---

*This solution leads to the orbital diamagnetism of free electrons (see, e.g., Seitz, 1940, Chapter XVI).

Carry out a perturbation analysis and show that if $\langle H_1 \rangle$ and $\langle H_2 \rangle$ represent the perturbations proportional to B and B^2 then whenever $\langle H_1 \rangle \neq 0$,

$$\langle H_2 \rangle \ll \langle H_1 \rangle \tag{51}$$

Derive expressions for diamagnetic and paramagnetic susceptibilities.

PROBLEM 18.14

In Problem 18.13 if we assume A to be given by Eq. (49) show that the final results are the same.

PROBLEM 18.15

The potential energy of a two dimensional harmonic oscillator can be written as

$$V = \tfrac{1}{2}\,\mu\omega_0^2\,(x^2 + y^2) \tag{52}$$

Show that the energy levels and wavefunctions of the oscillator placed in a uniform magnetic field along the z-direction are given by

$$E = \Big[\, 2n + |\,m\,| + 1 \,\Big]\,\hbar\left(\,\omega_0^2 + \frac{Q^2B^2}{4\mu^2}\,\right)^{\frac{1}{2}} - \frac{mQ\hbar B}{2\mu} \tag{53}$$

$$\psi = \exp\left[\, im\varphi - \frac{\varphi^2}{2b}\,\right]\left(\,\frac{\rho}{b}\,\right)^{|\,m\,|}\,{}_1F_1\left(\,-n,\,|\,m\,| + 1,\, \frac{\rho^2}{b^2}\,\right) \tag{54}$$

$$b = \left(\,\frac{q^2B^2}{4\hbar} + \frac{\mu^2\omega_0^2}{\hbar^2}\,\right)^{-1/4}$$

$$\rho^2 = x^2 + y^2$$

$$m = 0,\ \pm 1,\ \pm 2,\ \pm 3\ \ldots$$

$$n = 0,\ 1,\ 2,\ \ldots$$

SOLUTIONS

SOLUTION 18.1

The perturbation is

$$H' = \frac{\mu_B B}{\hbar}\,L_z = -i\mu_B B\,\frac{\partial}{\partial\varphi} \tag{55}$$

The eigenfunctions of H_0 are

$$u(n, l, m_l) = R_{nl}\,(r)\;Y_{lm_l}\,(0, \varphi) \tag{56}$$

Since $L_z\,Y_{lm_l} = m_l\hbar Y_{lm_l}$, we get

$$H'u\,(n, l, m_l) = m_l\,\hbar\,u\,(n, l, m_l) \tag{57}$$

and, consequently the off diagonal elements are zero*. The Zeeman splitting is therefore given by

$$\Delta = \int u^*(n, l, m_l)\, H' u(n, l, m_l)\, d\tau = \mu_B B m_l \tag{58}$$

Thus a level characterized by the orbital angular quantum number l splits up into $(2l + 1)$ levels. However, because of the selection rule

$$\Delta m_l = 0, \pm 1 \tag{59}$$

we get three lines of frequencies

$$\omega_0 - \frac{\mu_B B}{\hbar}, \quad \omega_0, \quad \omega_0 + \frac{\mu_B B}{\hbar} \tag{60}$$

which is known as the normal Zeeman effect (see also Sec. 21.5 and Fig. 21.4).

SOLUTION 18.2

Because of the spin-orbit interaction, the levels split and each level is characterized by definite values of J^2, L^2 and s^2 (see Problem 11.12); the corresponding Pauli wavefunctions are given by

$$\psi^{(0)}P = \begin{pmatrix} \left[\dfrac{l + \frac{1}{2} + m_j}{2l + 1}\right]^{\frac{1}{2}} R_{nl}(r) Y_{l,\, m_j - 1/2} \\ \left[\dfrac{l + \frac{1}{2} - m_j}{2l + 1}\right]^{\frac{1}{2}} R_{nl}(r) Y_{l,\, m_j - 1/2} \end{pmatrix}_{\text{for } j = l + \frac{1}{2}} \tag{61}$$

and

$$\psi^{(0)}P = \begin{pmatrix} -\left[\dfrac{l + \frac{1}{2} - m_j}{2l + 1}\right]^{\frac{1}{2}} R_{nl}(r) Y_{l,\, m_j + 1/2} \\ \left[\dfrac{l + \frac{1}{2} + m_j}{2l + 1}\right]^{\frac{1}{2}} R_{nl}(r) Y_{l,\, m_j + 1/2} \end{pmatrix}_{\text{for } j = l - \frac{1}{2}} \tag{62}$$

The states corresponding to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ are $(2l + 2)$ and $2l$-fold degenerate. Now, the Pauli operator for H'' is

$$(H'')_P = \frac{\mu_B B}{\hbar} \begin{pmatrix} L_z + \frac{1}{2} g\hbar & 0 \\ 0 & L_z - \frac{1}{2} g\hbar \end{pmatrix} \tag{63}$$

Since

$$L_z\, Y_{l,\, m_j - 1/2} = -i\hbar \frac{\partial}{\partial \varphi} Y_{l,\, m_j - 1/2} = (m_j - \tfrac{1}{2})\, \hbar\, Y_{l,\, m_j - 1/2}$$

we immediately have (for $j = l + \frac{1}{2}$)

$$(H'')_P\, (\psi^{(0)})_P = \mu_B B \begin{pmatrix} \left(\dfrac{l + \frac{1}{2} + m_j}{2l + 1}\right)^{\frac{1}{2}} (m_j - \frac{1}{2} + \frac{1}{2} g)\, R_{nl}\, Y_{l, m_j - 1/2} \\ \left(\dfrac{l + \frac{1}{2} - m_j}{2l + 1}\right)^{\frac{1}{2}} (m_j + \frac{1}{2} - \frac{1}{2} g)\, R_{nl}\, Y_{l, m_j + 1/2} \end{pmatrix}$$

*Indeed $u(n, l, m_l)$ are the *exact* eigenfunctions of $H (= H_0 + H')$ corresponding to the eigenvalue $E_n + \mu_B B m_l$.

The off-diagonal elements are obviously zero and the perturbation is thus given by

$$\Delta = \int (\psi^{(0)})_P (H'')_P (\psi^{(0)})_P \, d\tau$$

$$= \mu_B B \, \frac{(2l + g) \, m_j}{(2l + 1)} \qquad \text{for } j = l + \tfrac{1}{2} \tag{64}$$

and similarly,

$$\Delta = \mu_B B \, \frac{(2l + 2 - g) \, m_j}{(2l + 1)} \qquad \text{for } j = l - \tfrac{1}{2} \tag{65}$$

Thus the $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ split into $(2l + 2)$ and $2l$ levels. Further, if we assume $g = 2$, Equations (64) and (65) can be combined to give

$$\Delta = \mu_B B \, \frac{j + \frac{1}{2}}{l + \frac{1}{2}} \, m_j; \quad j = l \pm \tfrac{1}{2} \tag{66}$$

The factor $(j + \frac{1}{2})/(l + \frac{1}{2})$ is known as the Lande g-factor (see Fig. 21.5).

SOLUTION 18.3

It is obvious that the functions

$$| \, \psi \, (n, l, m_l, \tfrac{1}{2}) \, \rangle = | \, n, l, m_l, \hat{\mathbf{z}} \uparrow \, \rangle \tag{67}$$

and

$$| \, \psi \, (n, l, m_l, -\tfrac{1}{2}) \, \rangle = | \, n, l, m_l, \hat{\mathbf{z}} \downarrow \, \rangle \tag{68}$$

are the exact eigenfunctions of $H_0 + H''$ belonging to the eigenvalues

$$E_n + \frac{\mu_B B}{\hbar} \, [m_l \hbar + \tfrac{1}{2} g \hbar]$$

and

$$E_n + \frac{\mu_B B}{\hbar} \, [m_l \hbar - \tfrac{1}{2} g \hbar]$$

respectively. These equations can be combined to give

$$E_n + \mu_B B \, (m_l + 2m_s) \tag{69}$$

where $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$ correspond to the spin up and spin down states and we have assumed $g = 2$. Now, for the two states given by Eqs. (67) and (68), L_z and s_z are well defined and expectation values of L_x, s_x, L_y, and s_y are zero (see Problem 9.2). Thus the perturbation is given by

$$\langle \, f(r) \, \mathbf{L} \cdot \mathbf{s} \, \rangle = \langle \, f(r) \, \rangle \, \langle \, L_z \, s_z \, \rangle = \zeta_{n,l} \, m_l m_s \tag{70}$$

where

$$\zeta_{n,l} = \langle \, f(r) \, \rangle \, \hbar^2 = \frac{gZ\hbar\alpha\hbar^2}{4m^2c} \int_0^\infty \frac{1}{r^3} \, | \, R_{nl}(r) \, |^2 r^2 \, dr$$

$$= \frac{Z^4 \alpha^4 mc^2}{2n^3 \, l \, (l + \frac{1}{2}) \, (l + 1)} \tag{71}$$

and we have used Eq. (10) of Appendix J. Thus the energy levels are given by

$$E = E_n + \mu_B B \, (m_l + 2m_s) + \zeta_{n,l} \, m_l m_s \tag{72}$$

where

$$m_l = -l, \ldots, +l \quad \text{and} \quad m_s = +\tfrac{1}{2} \text{ and } -\tfrac{1}{2} \tag{73}$$

Equation (72) represents the Paschen-Back effect and as can be seen the operators L^2, s^2, L_z and s_z have well defined values for each state; this is referred to as by saying that L^2, s^2, L_z and s_z are good quantum numbers. The splitting for the *P*-states of an alkali atom is shown in Fig. 18.2. In the figure $\mathscr{B} = \mu_B B/\zeta_{n,l}$. At $\mathscr{B} = 0$, we have the fine structure splitting. For small values of $\mathscr{B}$, Eq. (66) is to be used and for large values of $\mathscr{B}$, Eq. (72) is to be used. Both equations are limiting forms of Eq. (81) which should be used for intermediate values of $\mathscr{B}$.

SOLUTION 18.4

We should first mention that for weak fields s^2, L^2, J^2 and J_z are good quantum numbers, and on the other hand, for strong fields s^2, L^2, L_z and s_z are good

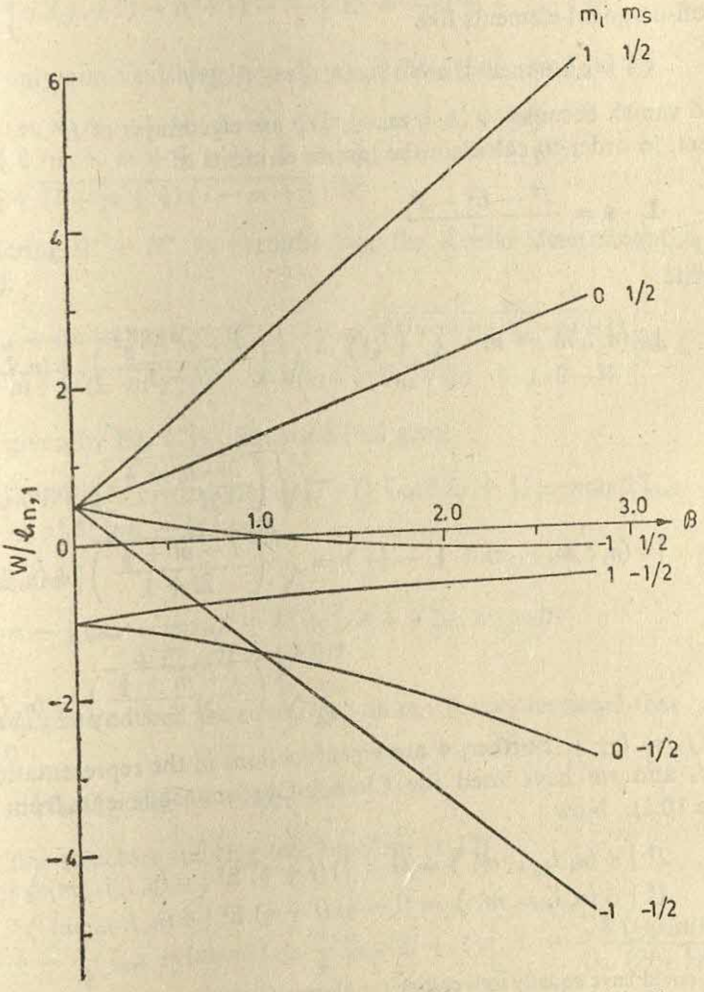

Fig. 18.2 The splitting of the *P*-state of an alkali atom by magnetic field. The two states corresponding to $B = 0$ represent the fine structure splitting.

quantum numbers. However, for intermediate fields neither of them are good quantum numbers and one must calculate the off-diagonal elements as is done in degenerate perturbation theory.

We choose as our representation, the eigenstates for the strong field case*; these are given by Eqs. (67) and (68). Now, from Eq. (72)

$$\begin{aligned}\langle \psi(n, l, m_l, \pm \tfrac{1}{2}) \mid H'' \mid \psi(n, l, m_l, \pm \tfrac{1}{2}) \rangle \\ = (m \pm \tfrac{1}{2})\, \mu_B B\end{aligned} \tag{74}$$

where**

$$m = m_l + m_s = \begin{cases} m_l + \frac{1}{2} & \text{for } m_s = \frac{1}{2} \\ m_l - \frac{1}{2} & \text{for } m_s = -\frac{1}{2} \end{cases}$$

The off-diagonal elements like

$$\langle \psi(n, l, m_l, \pm \tfrac{1}{2}) \mid H'' \mid \psi(n, l, m_l, \mp \tfrac{1}{2}) \rangle$$

would vanish because $|\psi(n, l, m_l, \pm \tfrac{1}{2})\rangle$ are eigenstates of H''.

Next, in order to calculate the matrix elements of

$$\mathbf{L} \cdot \mathbf{s} = \frac{J^2 - L^2 - s^2}{2} \tag{75}$$

we write

$$\begin{aligned}|\psi(n, l, m_l = m - \tfrac{1}{2}, + \tfrac{1}{2})\rangle &= \sqrt{\left(\frac{l + m + \frac{1}{2}}{2l + 1}\right)}\, |\phi(n, l, j_+, m)\rangle \\ &\quad - \sqrt{\left(\frac{l - m + \frac{1}{2}}{2l + 1}\right)}\, |\phi(n, l, j_-, m)\rangle\end{aligned} \tag{76}$$

$$\begin{aligned}|\psi(n, l, m_l = m + \tfrac{1}{2}, - \tfrac{1}{2})\rangle &= \sqrt{\left(\frac{l - m + \frac{1}{2}}{2l + 1}\right)}\, |\phi(n, l, j_+, m)\rangle \\ &\quad + \sqrt{\left(\frac{l + m + \frac{1}{2}}{2l + 1}\right)}\, |\phi(n, l, j_-, m)\rangle\end{aligned} \tag{77}$$

where $j_\pm = l \pm \frac{1}{2}$. Further, ϕ are eigenfunctions in the representation L^2, s^2, J^2 and J_z and we have used the Clebsch-Gordan coefficients from Chapter 10 (Table 10.1). Now

$$J^2 \mid \phi(n, l, j_+, m) \rangle = (l + \tfrac{1}{2})(l + \tfrac{3}{2})\, \hbar^2 \mid \phi(n, l, j_+, m) \rangle \tag{78}$$

$$J^2 \mid \phi(n, l, j_-, m) \rangle = (l - \tfrac{1}{2})(l + \tfrac{1}{2})\, \hbar^2 \mid \phi(n, l, j_-, m) \rangle \tag{79}$$

---

*We could have equally well chosen the eigenstates for the weak field case.

**The quantity m is denoted by m_j in Problem 18.2. For convenience, we are dropping the subscript j.

The operator L^2 has the eigenvalues $l(l+1)\hbar^2$ and s^2 has the eigenvalue $\frac{1}{2}(\frac{3}{2})\hbar^2 = \frac{3}{4}\hbar^2$. Thus (omitting the subscripts n, l)

$$\langle \psi(m_l = m - \tfrac{1}{2}, \tfrac{1}{2}) \mid \frac{J^2 - L^2 - s^2}{2} \mid \psi(m_l = m - \tfrac{1}{2}, \tfrac{1}{2})\rangle$$

$$= \left[\sqrt{\left(\frac{l+m+\frac{1}{2}}{2l+1}\right)}\langle \phi(j_+, m) \mid - \sqrt{\left(\frac{l-m+\frac{1}{2}}{2l+1}\right)}\langle \phi(j_-, m) \mid \right]$$

$$\frac{J^2 - L^2 - s^2}{2} \times \left[\sqrt{\left(\frac{l+m+\frac{1}{2}}{2l+1}\right)} \mid \phi(j_+, m)\rangle - \sqrt{\left(\frac{l-m+\frac{1}{2}}{2l+1}\right)} \mid \phi(j_-, m)\rangle\right]$$

$$= \frac{l+m+\frac{1}{2}}{2l+1}\,\frac{1}{2}\cdot\left\{j_+(j_+ + 1) - l(l+1) - \frac{3}{4}\right\}\hbar^2$$

$$+ \frac{l-m-\frac{1}{2}}{2l+1}\left\{j_-(j_- + 1) - l(l+1) - \frac{3}{4}\right\}\hbar^2 = \frac{1}{2}\left(m - \frac{1}{2}\right)\hbar^2$$

Further, the only non-vanishing, non-diagonal matrix elements are

$$\begin{aligned} &\langle \psi(m_l = m - \tfrac{1}{2}, \tfrac{1}{2}) \mid \mathbf{L}\cdot\mathbf{s} \mid \psi(m_l = m + \tfrac{1}{2}, -\tfrac{1}{2})\rangle \\ &= \langle \psi(m_l = m + \tfrac{1}{2}, -\tfrac{1}{2}) \mid \mathbf{L}\cdot\mathbf{s} \mid \psi(m_l = m - \tfrac{1}{2}, \tfrac{1}{2})\rangle \\ &= \tfrac{1}{2}\sqrt{(l + m + \tfrac{1}{2})(l - m + \tfrac{1}{2})}\,\hbar^2 \end{aligned}$$

Thus, considering $H' + H''$ as perturbation, the secular determinant is (see Section 11.3):

$$\begin{vmatrix} \frac{1}{2}(m-\frac{1}{2})\zeta_{n,l} + (m+\frac{1}{2})\mu_B B - W & \frac{1}{2}\zeta_{n,l}\sqrt{(l+m+\frac{1}{2})(l-m+\frac{1}{2})} \\ \frac{1}{2}\zeta_{n,l}\sqrt{(l+m+\frac{1}{2})(l-m+\frac{1}{2})} & -\frac{1}{2}(m+\frac{1}{2})\zeta_{n,l} + (m-\frac{1}{2})\mu_B B - W \end{vmatrix} = 0 \quad (80)$$

where $\zeta_{n,l}$ is given by Eq. (71). Equation (80) gives

$$W^2 + W[\tfrac{1}{2}\zeta_{n,l} - 2m\mu_B B] + [-(\tfrac{1}{2}\zeta_{n,l})^2 l(l+1) - m\mu_B B\zeta_{n,l} + \mu_B^2 B^2(m^2 - \tfrac{1}{4})] = 0$$

The solutions are

$$W = -\tfrac{1}{4}\zeta_{n,l} + m_j\mu_B B \pm \tfrac{1}{4}[4\mu_B^2 B^2 + 8\zeta_{n,l} m_j \mu_B B + \zeta_{n,l}^2(2l+1)^2]^{1/2} \quad (81)$$

where we have reintroduced the subscript j on m. It may be noted that

(i) for $B = 0$

$$W = \tfrac{1}{4}\zeta_{n,l}[-1 \pm (2l+1)] \quad (82)$$

which is the fine structure splitting (see Problem 11.12)

(ii) for small B

$$W \to -\frac{1}{4}\zeta_{n,l} + (m\mu_B B) \pm \frac{1}{4}\zeta_{n,l}(2l+1)\left[1 + \frac{8(m\mu_B B)}{\zeta_{n,l}(2l+1)^2}\right]^{\frac{1}{2}}$$

$$\approx \frac{1}{4}\zeta_{n,l}[-1 \pm (2l+1)] + \frac{2l+1\pm 1}{2l+1}m_j\mu_B B \quad (83)$$

which is the Zeeman effect (see Problem 18.2)
(iii) for large B

$$\begin{aligned} W &\rightarrow -\frac{1}{4}\zeta_{n,l} + m\mu_B B \pm \frac{1}{2}\mu_B B\left[1 + \frac{m_j\zeta_{n,l}}{\mu_B B}\right]^{\frac{1}{2}} \\ &\simeq \left[-\tfrac{1}{4} \pm \tfrac{1}{2} m_j\right]\zeta_{n,l} + \left(m_j \pm \tfrac{1}{2}\right)\mu_B B \end{aligned} \tag{84}$$

which is the same as given by Eq. (72) provided we note that $m_j = m_l + m_s$ and the upper and lower signs in Eq. (84) correspond to $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$ respectively.

For the P-state of an alkali atom, $l = 1$, and we may write Eq. (81) in the form

$$\frac{W}{\zeta_{n,l}} = -\frac{1}{4} + m_j\mathscr{B} \pm \frac{1}{4}\sqrt{4\mathscr{B}^2 + 8m_j\mathscr{B} + 9} \tag{85}$$

where $\mathscr{B} = \mu_B B/l_{n,l}$. In Fig. 18.2 we have plotted the splitting of the P-state of an alkali atom.

SOLUTION 18.5

We first note that

$$\sigma_x \mid \uparrow\rangle = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \mid \downarrow\rangle$$

and

$$\sigma_y \mid \uparrow\rangle = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = i \mid \uparrow\rangle$$

where $\mid \uparrow\rangle$ and $\mid \downarrow\rangle$ states are the $\mid \hat{z}\uparrow\rangle$ and $\mid \hat{z}\downarrow\rangle$ states. Similarly,

$$\sigma_x \mid \downarrow\rangle = \mid \uparrow\rangle \quad \text{and} \quad \sigma_y \mid \downarrow\rangle = -i \mid \uparrow\rangle$$

since the components of σ_e operate only on the electron spin state and the components of σ_p operate only on the proton spin state we have, for example,

$$\begin{aligned} \sigma_{ex}\sigma_{px} \mid e\uparrow p\downarrow\rangle &= \sigma_{ex} \mid e\uparrow p\uparrow\rangle = \mid e\downarrow p\uparrow\rangle \\ \sigma_{ey}\sigma_{py} \mid e\uparrow p\downarrow\rangle &= -i\sigma_{ey} \mid e\uparrow p\uparrow\rangle = \mid e\downarrow p\uparrow\rangle \\ \sigma_{ez}\sigma_{pz} \mid e\uparrow p\downarrow\rangle &= -\sigma_{ez} \mid e\uparrow p\downarrow\rangle = -\mid e\uparrow p\downarrow\rangle \end{aligned}$$

Thus

$$\begin{aligned} \sigma_e \cdot \sigma_p \mid e\uparrow p\downarrow\rangle &= \sigma_{ex}\sigma_{px} \mid e\uparrow p\downarrow\rangle + \sigma_{ey}\sigma_{py} \mid e\uparrow p\downarrow\rangle + \sigma_{ez}\sigma_{pz} \mid e\uparrow p\downarrow\rangle \\ &= 2 \mid e\downarrow p\uparrow\rangle - \mid e\uparrow p\downarrow\rangle \end{aligned}$$

Therefore

$$P \mid e\uparrow p\downarrow\rangle = \tfrac{1}{2}[1 + \sigma_e \cdot \sigma_p] \mid e\uparrow p\downarrow\rangle = \mid e\downarrow p\uparrow\rangle$$

Similarly one can consider other operations to obtain

$$P \mid e\uparrow p\uparrow\rangle = \mid e\uparrow p\uparrow\rangle, \; P \mid e\downarrow p\downarrow\rangle = \mid e\downarrow p\downarrow\rangle$$

and

$$P \mid e\downarrow p\uparrow\rangle = \mid e\uparrow p\downarrow\rangle \tag{86}$$

which shows that P is the spin exchange operator.

SOLUTION 18:6

Since H' is proportional to $\sigma_e \cdot \sigma_p$, we have to look for a representation in which $\sigma_e \cdot \sigma_p$ is diagonal. Introducing the angular momentum operators

$$\mathbf{s}_1 = \tfrac{1}{2}\hbar\,\sigma_e,\ \mathbf{s}_2 = \tfrac{1}{2}\hbar\,\sigma_p \qquad \text{and} \qquad \mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 \tag{87}$$

we have

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \tfrac{1}{4}\hbar^2\,\sigma_e \cdot \sigma_p = \tfrac{1}{2}\left[S^2 - s_1^2 - s_2^2\right] \tag{88}$$

We have to look for a representation in which S^2, s_1^2 and s_2^2 are diagonal. This is easily obtained from the Clebsch-Gordan coefficients (see Table 10.1 and Sec. 10.3) and one has the four states

$$\left.\begin{aligned} |1\rangle &= |e\uparrow p\uparrow\rangle \\ |2\rangle &= |e\downarrow p\downarrow\rangle \\ |3\rangle &= \frac{1}{\sqrt{2}}\left[|e\uparrow p\downarrow\rangle + |e\downarrow p\uparrow\rangle\right] \end{aligned}\right\} \tag{89}$$

$$|4\rangle = \frac{1}{\sqrt{2}}\left[|e\uparrow p\downarrow\rangle - |e\downarrow p\uparrow\rangle\right] \tag{90}$$

The first three states represent the triplet state and the fourth state represents the singlet state. For the triplet state the values of S^2, s_1^2 and s_2^2 are $2\hbar^2$, $\frac{3}{4}\hbar^2$ and $\frac{3}{4}\hbar^2$ respectively; the corresponding values for the singlet state are 0, $\frac{3}{4}\hbar^2$ and $\frac{3}{4}\hbar^2$ respectively. Thus the values of $\mathbf{s}_1 \cdot \mathbf{s}_2$; are

$$\tfrac{1}{2}\left[2 - \tfrac{3}{4} - \tfrac{3}{4}\right]\hbar^2 = \tfrac{1}{4}\hbar^2 \qquad \text{for the triplet state}$$

and

$$\tfrac{1}{2}\left[-\tfrac{3}{4} - \tfrac{3}{4}\right]\hbar^2 = -\tfrac{3}{4}\hbar^2 \qquad \text{for the singlet state}$$

Consequently, for $n = 1$, the enegry for the triplet and singlet states are

$$E_1 + \epsilon \qquad \text{and} \qquad E_1 - 3\epsilon \tag{91}$$

The separation is

$$4\epsilon = \frac{32}{3a_0^3}\left(g_p \frac{q\hbar}{4M_p}\right)\left(g\,\frac{q\hbar}{4m}\right) \tag{92}$$

the corresponding wavelength ($= hc/4\epsilon$) is about 21 cm which is the famous *21 cm line* used by radio astronomers to measure the amount of hydrogen in the galaxy. The measured value of the frequency is (quoted from Feynman, 1965)

$$\nu = (1420405751.800 \pm .028)\ \text{Hz}$$

which is one of the most accurately determined quantities.

Solution 18.7

The states $| e \uparrow p \uparrow \rangle$ and $| e \downarrow p \downarrow \rangle$ are eigenstates of H' belonging to the eigenvalues

$$\mu_B B - \mu_p B + \epsilon$$

and

$$-\mu_B B + \mu_p B + \epsilon$$

It is easy to see that $| e \uparrow p \downarrow \rangle$ and $| e \downarrow p \uparrow \rangle$ are not eigenstates. We write

$$| a \rangle = | e \uparrow p \downarrow \rangle \quad \text{and} \quad | b \rangle = | e \downarrow p \uparrow \rangle$$

Now

$$H' \, | a \rangle = H' \, | e \uparrow p \downarrow \rangle = \mu_B B \, | e \uparrow p \downarrow \rangle + \mu_p B \, | e \uparrow p \downarrow \rangle + \epsilon \, (2P - 1) \, | e \uparrow p \downarrow \rangle = (\mu_B B + \mu_p B - \epsilon) \, | a \rangle + 2\epsilon \, | b \rangle$$

Thus

$$\langle a \, | \, H' \, | \, a \rangle = (\mu_B B + \mu_p B - \epsilon), \quad \langle b \, | \, H' \, | \, a \rangle = 2\epsilon$$

Similarly

$$\langle b \, | \, H' \, | \, b \rangle = (-\mu_B B - \mu_p B - \epsilon), \; \langle a \, | \, H' \, | \, b \rangle = 2\epsilon$$

The secular determinant is

$$\begin{vmatrix} \langle a \, | \, H' \, | \, a \rangle - W & \langle b \, | \, H' \, | \, a \rangle \\ \langle a \, | \, H' \, | \, b \rangle & \langle b \, | \, H' \, | \, b \rangle - W \end{vmatrix} = 0$$

Which gives

$$W = -\epsilon \pm \sqrt{4\epsilon^2 + (\mu_B + \mu_p)^2 B^2} \tag{93}$$

the corresponding wavefunctions can easily be found. For $B \to 0$ we get the results of the previous problem.

Solution 18.8

The Hamiltonian is

$$H_0 = \frac{gq}{2m} \mathbf{s} \cdot \mathbf{B} = \frac{1}{2} \hbar \omega_0 \sigma_z \tag{94}$$

where we have intentionally put a subscript to H (so that we can use the same notation in Problem 18.10) and

$$\omega_0 = \frac{gqB_0}{2m} \cong \frac{\mu_B B_o}{\hbar} \tag{95}$$

The eigenvalues of H are $+\frac{1}{2} \hbar\omega_0$ and $-\frac{1}{2} \hbar\omega_0$, the corresponding eigenkets being $| \hat{z} \uparrow \rangle$ and $| \hat{z} \downarrow \rangle$ respectively. Thus the general solution of the

Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\,|\,\Psi(t)\rangle = H_0\,|\,\Psi(t)\rangle$$

is

$$|\,\Psi(t)\rangle = c_1\exp(-i\omega_0 t/2)\,|\,\hat{z}\uparrow\rangle + c_2\exp(+i\omega_0 t/2)\,|\,\hat{z}\downarrow\rangle$$

But

$$\left.\begin{aligned} |\,\hat{z}\uparrow\rangle &= \frac{1}{\sqrt{2}}\Big[\,|\,\hat{x}\uparrow\rangle + |\,\hat{x}\downarrow\rangle\Big] \\ \text{and}\quad |\,\hat{z}\downarrow\rangle &= \frac{1}{\sqrt{2}}\Big[\,|\,\hat{x}\uparrow\rangle - |\,\hat{x}\downarrow\rangle\Big] \end{aligned}\right\} \tag{96}$$

Thus

$$|\,\Psi(t)\rangle = \cos\frac{\omega_0 t}{2}\,|\,\hat{x}\uparrow\rangle - i\sin\frac{\omega_0 t}{2}\,|\,\hat{x}\downarrow\rangle \tag{97}$$

where we have assumed that at $t = 0$, the spin is in the x-direction, i.e., $|\,\Psi(0)\rangle = |\,\hat{x}\uparrow\rangle$ which gives $c_1 = c_2 = 1/\sqrt{2}$. The expectation value of s_x is given by

$$\langle s_x\rangle = \langle\Psi(t)\,|\,s_x\,|\,\Psi(t)\rangle = \tfrac{1}{2}\,\hbar\cos\omega_0 t \tag{98}$$

Similarly

$$\langle s_y\rangle = \langle\Psi(t)\,|\,s_y\,|\,\Psi(t)\rangle = -\tfrac{1}{2}\,\hbar\sin\omega_0 t \tag{99}$$

$$\langle s_z\rangle = \langle\Psi(t)\,|\,s_z\,|\,\Psi(t)\rangle = 0 \tag{100}$$

The above equations physically imply that the direction of spin rotates about the z-axis* with angular velocity ω_0.

It is interesting to note that the Schrödinger equation can be integrated to give

$$|\,\Psi(t)\rangle = \exp(-iH_0 t/\hbar)\,|\,\Psi(0)\rangle = \exp(-i\omega_0 t\sigma_z/2\,|\,\Psi(0)\rangle \tag{101}$$

SOLUTION 18.9

In the Heisenberg representation (see Sec. 8.12)

$$\left.\begin{aligned} i\hbar\frac{ds_x}{dt} &= [s_x, H] = \omega_0\,[s_x, s_z] = -\,i\hbar\omega_0 s_y(t) \\ i\hbar\frac{ds_y}{dt} &= [s_y, H] = \omega_0\,[s_y, s_z] = +\,i\hbar\omega_0 s_x(t) \\ i\hbar\frac{ds_z}{dt} &= 0 \end{aligned}\right\} \tag{102}$$

---

*It is because of this precessional motion that in the Stern-Gerlach experiment (see Sec. 9.4), the component of μ along the direction of the field remains constant and μ_x and μ_y average out to zero. Thus the force acting on the atom (averaged over the oscillations) is simply $\nabla(\mu_z B_z)$.

Thus

$$\frac{d^2 s_x}{dt^2} = -\omega_0 \frac{ds_y}{dt} = -\omega_0^2 s_x \tag{103}$$

The solutions are therefore

$$s_x(t) = s_x(0)\cos\omega_0 t + s_y(0)\sin\omega_0 t \tag{104}$$
$$s_y(t) = -s_x(0)\sin\omega_0 t + s_y(0)\cos\omega_0 t \tag{105}$$
$$s_z(t) = s_z(0) \tag{106}$$

The expectation values are

$$\langle s_x(t)\rangle = \langle \Psi(0) \mid s_x(t) \mid \Psi(0)\rangle = \langle s_x(0)\rangle \cos\omega_0 t + \langle s_y(0)\rangle \sin\omega_0 t \tag{107}$$

etc. For $\mid\Psi(0)\rangle = \mid\hat{x}\uparrow\rangle$

$$\langle s_x(0)\rangle = \tfrac{1}{2}\hbar,\ \langle s_y(0)\rangle = 0 = \langle s_z(0)\rangle \tag{108}$$

and we obtain the same result as in the previous problem. For

$$\mid\Psi(0)\rangle = \cos\frac{\varphi}{2}\mid\hat{z}\uparrow\rangle + \sin\frac{\varphi}{2}\mid\hat{z}\downarrow\rangle \tag{109}$$

$$s_x(0)\mid\Psi(0)\rangle = \tfrac{1}{2}\hbar\cos\frac{\varphi}{2}\,\sigma_x\binom{1}{0} + \tfrac{1}{2}\hbar\sin\frac{\varphi}{2}\,\sigma_x\binom{0}{1}$$

$$= \tfrac{1}{2}\hbar\cos\frac{\varphi}{2}\mid\hat{z}\downarrow\rangle + \tfrac{1}{2}\hbar\sin\frac{\varphi}{2}\mid\hat{z}\uparrow\rangle$$

Thus

$$\langle s_x(0)\rangle = \tfrac{1}{2}\hbar\sin\varphi$$

Similarly $\langle s_y(0)\rangle = 0$ and $\langle s_z(0)\rangle = \frac{1}{2}\hbar\cos\varphi$. Physically this implies that at $t = 0$, the spin is in the $x-z$ plane at an angle φ with the z-axis. Using Eqs. (104)–(106), we get

$$\langle s_x(t)\rangle = \tfrac{1}{2}\hbar\sin\varphi\cos\omega_0 t \tag{110}$$
$$\langle s_y(t)\rangle = -\tfrac{1}{2}\hbar\sin\varphi\sin\omega_0 t \tag{111}$$
$$\langle s_z(t)\rangle = \tfrac{1}{2}\hbar\cos\varphi \tag{112}$$

which shows the precessional motion.

SOLUTION 18.10

The Hamiltonian is

$$H = H_0 + H'$$

where H_0 is given by Eq. (94) and

$$H' = \frac{gq\hbar}{4m}B\,[\sigma_x\cos\omega t + \sigma_y\sin\omega t] \simeq \mu_B B\,[\sigma_x\cos\omega t + \sigma_y\sin\omega t] \tag{113}$$

Our objective is to solve the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\mid\Psi(t)\rangle = (H_0 + H')\mid\Psi(t)\rangle \tag{114}$$

and since H' now depends on time we adopt the method used in Sec. 20.2. The eigenkets of H_0 are $|\hat{\mathbf{z}}\uparrow\rangle$ and $|\hat{\mathbf{z}}\downarrow\rangle$ (see Solution 18.8) which we denote by $|1\rangle$ and $|2\rangle$, the corresponding energy eigenvalues being $E_1\ (= \frac{1}{2}\hbar\,\omega_0)$ and $E_2\ (= -\frac{1}{2}\hbar\,\omega_0)$ · We write [cf. Eq. (5) of Chapter 20]

$$|\Psi(t)\rangle = \sum_{n=1,2} C_n(t)\,|n\rangle \exp\,(-iE_nt/\hbar) \tag{115}$$

and obtain [see Eq. (9) of Chapter 20]

$$i\hbar\frac{dC1}{dt} = C_1(t)\,\mu_B B_1\,[\cos\omega t\,\langle 1\,|\,\sigma_x\,|\,1\rangle + \sin\omega t\,\langle 1\,|\,\sigma_y\,|\,1\rangle]$$

$$+ C_2(t)\,\mu_B B_1\,[\cos\omega t\,\langle 1\,|\,\sigma_x\,|\,2\rangle + \sin\omega t\,\langle 1\,|\,\sigma_y\,|\,2\rangle]\,e^{-i(E_2-E_1)t/\hbar}$$

or

$$i\,\frac{dC_1}{dt} = \omega_1\,C_2(t)\exp i\,(\omega_0-\omega)\,t \tag{116}$$

where $\omega_0 \simeq \mu_B B_0/\hbar$ [see Eq. (95)]. Similarly

$$i\,\frac{dC_2}{dt} = \omega_1\,C_1(t)\exp - i\,(\omega_0-\omega)\,t \tag{117}$$

where $\omega_1 = \mu_B B_1/\hbar$. Simple algebra gives

$$\frac{d^2C_2}{dt^2} - 2i\Delta\,\frac{dC_2}{dt} + \omega_1^2\,C_2(t) = 0 \tag{118}$$

where $\Delta = (\omega-\omega_0)/2$. The solution is

$$C_2(t) = A_1\,e^{i[\Delta+\Gamma]t} + A_2\,e^{i[\Delta-\Gamma]t} \tag{119}$$

where

$$\Gamma = \left[\left(\frac{\omega-\omega_0}{2}\right)^2 + \omega_1^2\right]^{1/2} = [\Delta^2+\omega_1^2]^{1/2}$$

Assuming that at $t=0$, the spin is pointing upwards, i.e.

$$C_1(0) = 1 \quad \text{and} \quad C_2(0) = 0$$

we get

$$C_2(t) = A\,e^{i\Delta t}\sin\Gamma t$$

Thus, using Eq. (117),

$$C_1(t) = \frac{iA}{\omega_1}\,[\Gamma\cos\Gamma t + i\Delta - \sin\Gamma t]e^{-i\Delta t/2}$$

Since $C_1(0) = 1$, we get $A = -i\omega_1/\Gamma$ giving

$$|C_2(t)|^2 = \frac{\omega_1^2}{\Delta^2 + \omega_1^2}\sin^2(\Gamma t) \tag{120}$$

Equation (120) represents the probability of spin-flip; it oscillates between zero and $\omega_1^2/(\Delta^2 + \omega_1^2)$, the maximum value occurring at

$$t = \frac{\pi}{2\Gamma}, \frac{3\pi}{2\Gamma}, \ldots$$

For $(\Delta/\omega_1) \geqslant 1$, the spin-flip probability is small; however at resonance $\omega = \omega_0$ and spin flips with certainty. The importance of such a phenomenon is discussed in Sec. 18.6.

SOLUTION 18.11

Equation (20) with $\phi = 0$, $Q = -q$ and **A** given by Eq. (49) becomes

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[E + \frac{iq\hbar}{2m}Bx\frac{\partial\psi}{\partial y} - q^2\frac{B^2x^2}{2m}\right]\psi = 0 \tag{121}$$

The solution of Eq. (121) is of the form

$$\psi(x) = u(x)\exp\left[\frac{i}{\hbar}(P_y y + P_z z)\right] \tag{122}$$

where $u(x)$ satisfies the equation

$$\frac{d^2u(x)}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{P_z^2}{2m} - \frac{q^2B^2}{2m}\left(x + \frac{P_y}{qB}\right)^2\right]u(x) = 0 \tag{123}$$

Equation (123) is very similar to the linear harmonic oscillator problem (see Secs. 3.6.3 and 11.2.3). The energy eigenvalues are

$$E = \frac{P_z^2}{2m} + \left(n + \frac{1}{2}\right)\hbar\,\frac{qB}{m} = \frac{P_z^2}{2m} + (2n+1)\,\mu_B B \tag{124}$$

where $n = 0, 1, 2, \ldots$ The corresponding $u(x)$ are the Hermite-Gauss functions. Notice that Eq. (124) is independent of P_y and hence there is infinite degeneracy. If spin angular momentum is also taken into account, we would get

$$E = \frac{P_z^2}{2m} + \left(2n + 1 \pm \frac{1}{2}\right)\mu_B B \tag{125}$$

SOLUTION 18.13

Equation (20) [for $Q = -q$ and **A** given by Eq. (50)] gives the following expression for the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r) - \frac{iq\hbar B}{2m}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) + \frac{q^2B^2}{8m}(x^2 + y^2)$$
$$= H_0 + H_1 + H_2 \tag{126}$$

where

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \tag{127}$$

$$H_1 = \frac{qB}{2m}L_z \tag{128}$$

$$H_2 = \frac{q^2B^2}{8m}(x^2 + y^2) \tag{129}$$

The term H_1 represents the interaction between the magnetic moment of the atom and the external magnetic field and gives rise to paramagnetism. The term H_2 can be interpreted as the interaction of the magnetic moment induced in the atom with the magnetic field (see, e.g., Dekker 1952, Sec. 18.3); this gives rise to diamagnetism. Treating H_1 and H_2 as perturbations we get

$$\langle H_1\rangle = \frac{qB}{2m}m_l\hbar = m_l\mu_B B \tag{130}$$

and

$$\langle H_2\rangle = \frac{q^2B^2}{8m}\langle r^2\sin^2\theta\rangle \tag{131}$$

If $\langle H_1\rangle \neq 0$ then (assuming $m_l \sim 1$)

$$\frac{\langle H_2\rangle}{\langle H_1\rangle} \simeq \frac{qB}{4\hbar}\langle r^2\sin^2\theta\rangle \sim \frac{qB}{4\hbar}a_0^2$$

where a_0 ($\simeq 0.5\times10^{-10}$ m) represents the Bohr radius. Thus

$$\frac{\langle H_2\rangle}{\langle H_1\rangle} \sim \frac{1.6\times10^{-19}}{4\times10^{-34}}\times0.25\times10^{-20}B$$

$$\sim 10^{-5}B \text{ (}B\text{ measured in tesla)}$$

$$\sim 10^{-9}B \text{ (}B\text{ measured in Gauss)}$$

Since the laboratory magnetic fields almost never exceed 10^5 Gauss,

$$\frac{\langle H_2\rangle}{\langle H_1\rangle} \ll 1 \tag{132}$$

hence whenever the paramagnetic term is non-zero, it dominates over the diamagnetic term. Thus for $l > 0$, $\langle H_1\rangle$ dominates and for $l = 0$, the diamagnetic term determines the magnetic behaviour. Indeed, for such a case $\langle\sin^2\theta\rangle = 2/3$ and

$$\langle H_2\rangle = \frac{q^2B^2}{12m}\langle r^2\rangle \tag{133}$$

The induced magnetic moment is therefore $-(q^2/6m)\langle r^2\rangle B$; thus if there are N

atoms per unit volume with each atom having z electrons, we get the following expression for the diamagnetic susceptibility

$$\chi_{dia} = -\frac{NZq^2}{6m}\langle r^2\rangle \tag{134}$$

consistent with the classical result (see, e.g., Dekker, 1952, Sec. 18.3). The diamagnetic susceptibility therefore depends on the charge distribution in the atoms. For further details and comparison with experimental data, see, e.g., Van Vleck (1932). In order to calculate the paramagnetic susceptibility, we note that the magnetic moment per unit volume, P, is the statistical average over all possible states.

$$\begin{aligned} P &= N\frac{\Sigma m_l\,\mu_B \exp[-\Gamma m_l]}{\Sigma \exp[-\Gamma m_l]} \\ &= N\mu_B\frac{\Sigma m_l(1-\Gamma m_l+\ldots)}{\Sigma(1-\Gamma m_l+\ldots.)} \approx -N\mu_B\left(\frac{N\mu_B}{kT}\right)\frac{1}{3}l(l+1) \end{aligned} \tag{135}$$

where N represents the number of atoms per unit volume and the summation over m_l goes from $-l$ to $+l$. Further,

$$\Gamma = \frac{\mu_B B}{kT}$$

which has been assumed to be very small compared to unity and use has been made of the relation

$$\sum_{m_l=-l}^{+l} m_l = 0, \qquad \sum_{m_l=-l}^{+l} m_l^2 = \tfrac{1}{3}\,l(l+1)(2l+1)$$

Thus

$$\chi_{para} = \frac{N\mu_B^2}{3kT}\,l(l+1) \tag{136}$$

If we take into account the effect of spin in a multi-electron atom, m_l has to be replaced by $M_l + 2M_s$ to obtain

$$\begin{aligned} \chi &= \frac{N\mu_B^2}{kT}\left[\frac{\Sigma M_l^2}{2L+1} + \frac{4\Sigma M_s^2}{2S+1}\right] \\ &= \frac{N\mu_B^2}{3kT}\left[L(L+1) + 4S(S+1)\right] \end{aligned} \tag{137}$$

The $1/T$ dependence of the susceptibility [see, Eqs. (136) and (137)] is known as the Curie law. For further details, see Van Vleck (1932).

CHAPTER 19

Elementary Theory of Scattering

19.1 Introduction

In some of the earlier chapters (e.g., Chapters 3 and 5) we had considered solutions of the Schrödinger equation which correspond to bound state problems where the wavefunction vanished at large distances from the origin; the corresponding energy levels were found to form a discrete set. In this chapter we will consider solutions of the Schrödinger equation where the energy eigenvalues would be continuously distributed; for such a case the wavefunction would not vanish at large distances from the origin. Such solutions correspond to the scattering of a particle by a force field where the energy is specified in advance and the behaviour of the wavefunction is found in terms of energy. We should mention here that in Chapter 4 we did consider the scattering by a one dimensional force field, the corresponding three dimensional case will be considered here.

Scattering experiments have provided most of the information about interactions among atoms, nuclei and particles. The general technique is to have a collimated beam of projectiles (particles) with well defined energies and sometimes other properties, such as polarization, as well. The particles are then scattered by a target of atoms and the scattered particles are detected by means of a suitable detector. The measurement could be simply the intensity variation as a function of angle or could involve more detailed information like the change in the energy or the polarization state, etc. The most commonly used parameter which displays the results of a scattering experiment is the cross-section. In Sec. 19.2 we will give the definition of the scattering cross-section according to classical mechanics which will be followed by the corresponding quantum mechanical definition. As mentioned earlier, scattering experiments provide information about interaction among atoms, nuclei and particles. Assuming a certain model for the interaction, one calculates the cross-section which is compared with experimental data. A good agreement between theory and experiment would suggest the validity of the model assumed. However, sometimes a variety of models give good agreement between theory and experiment and it becomes difficult to justify a particular model. In Secs. 19.4-19.6 we will develop theoretical methods to calculate the cross-section and wherever possible, comparison will be made with available experimental data.

19.2 The Classical Definition of Scattering Cross-section

We first give the definition of the scattering cross-section accroding to classical mechanics. We consider a beam of particles moving along the z-direction with a flux of I_0 particles per unit area per unit time. The particles undergo scattering by a potential and one measures the angular distribution of scattered particles.

The scattering cross-section $\sigma(\theta, \varphi)$ is defined by

$$\sigma(\theta, \varphi) d\Omega = \frac{\text{Number of particles scattered into solid angle } d\Omega \text{ per unit time}}{\text{Incident Intensity } I_0} \tag{1}$$

where $d\Omega$ represents an infinitesimal solid angle in the direction (θ, φ); the angle θ represents the angle of scattering and φ represents the azimuthal angle; the origin has been assumed to be at the centre of the force (see Fig. 19.1). For a spherically symmetric potential, $\sigma(\theta, \varphi)$ will be independent of φ.

The total cross-section is given by

$$\sigma = \iint \sigma(\theta, \varphi)\, d\Omega = \int_0^{\pi}\int_0^{2\pi} \sigma(\theta, \varphi) \sin\theta \, d\theta \, d\varphi \tag{2}$$

Thus σI_0 will represent the number of particles scattered out of the beam per unit time. For a spherically symmetric potential

$$\sigma = 2\pi \int_0^{\pi} \sigma(\theta) \sin\theta \, d\theta \tag{3}$$

In classical mechanics, each particle has a well defined trajectory and if we assume that all particles of the incident beam have the same speed v_0, there is an unique angle of scattering θ corresponding to a particular value of the impact parameter s. For example, for an attractive square well potential defined by

$$\begin{aligned} V(r) &= -V_0 \qquad 0 < r < a \\ &= 0 \qquad\quad\; r > a \end{aligned} \tag{4}$$

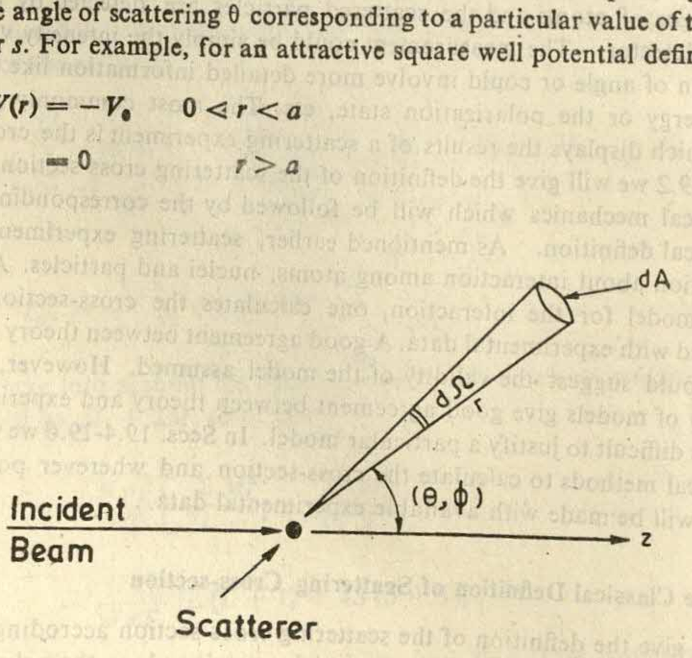

Fig. 19.1 The scattering of an incident beam. The particles scattered into the solid angle $d\Omega$ are received by the detector

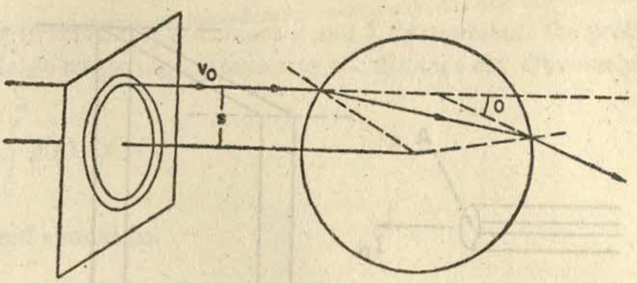

Fig. 19.2 The classical trajectory of a particle scattered by a square well potential, *s* denotes the impact parameter

the relation between the impact parameter *s* and the scattering angle θ is given by (see Fig. 19.2 and Problem 19.20).

$$\begin{aligned} \theta &= -2(i-r) = 2\left[\sin^{-1}\left(\frac{s}{na}\right) - \sin^{-1}\left(\frac{s}{a}\right)\right] && \text{for } 0 < s < a \\ &= 0 && \text{for } s > a \end{aligned} \tag{5}$$

where

$$n = \left[\frac{E+V_0}{E}\right]^{\frac{1}{2}} \quad \text{and } E = \tfrac{1}{2}\, m\, v_0^2 \tag{6}$$

Now, the number of particles which cross the annular area between s and $s + ds$ is $I\, 2\pi s\, ds$ and this must represent the number of particles scattered between θ and $\theta + d\theta$ which from Eq. (1) is simply $\sigma(\theta)\, I\, 2\pi \sin\theta\, d\theta$. Thus

$$I\, 2\pi s\, ds = -\sigma(\theta)\, I\, 2\pi \sin\theta\, d\theta$$

or

$$\sigma(\theta) = -\frac{s}{\sin\theta}\,\frac{ds}{d\theta} \tag{7}$$

where the negative sign is due to the fact that θ decreases with increase in the value of the impact parameter *s*. Equation (7) is quite general, if we now use the result given by Eq. (5) we would obtain

$$\sigma(\theta) = \frac{n^2a^2}{4\cos\dfrac{\theta}{2}}\;\frac{\left(n\cos\dfrac{\theta}{2} - 1\right)\left(n - \cos\dfrac{\theta}{2}\right)}{\left[1 + n^2 - 2n\cos\dfrac{\theta}{2}\right]^2} \tag{8}$$

Since no scattering occurs for $s > a$, we must have

$$\theta < \left[\pi - 2\sin^{-1}\left(\frac{1}{n}\right)\right] \tag{9}$$

In a similar manner one can calculate the scattering cross-section for other forms of $V(r)$ (see e.g., Goldstein, 1951, Chapter 3).

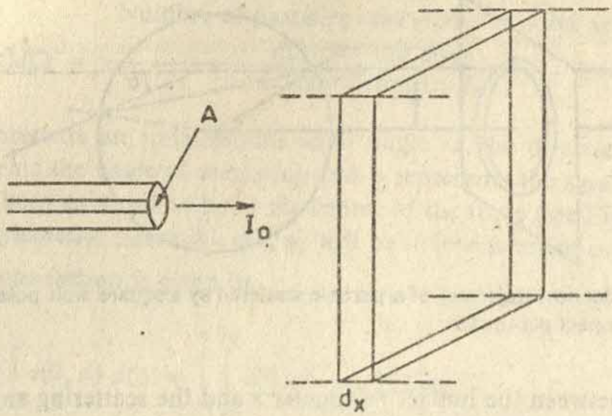

Fig. 19.3 A beam of particles of cross-sectional area A (and intensity I_0) incident normally on a target

19.2.1 Physical Interpretation of the Cross-Section

Let us consider a beam of particles of cross-sectional area A (and intensity I_0) incident normally on a target as shown in Fig. 19.3. Let there be N scatterers per unit volume inside the target. If $I(x)$ represents the intensity of beam after penetrating through a distance x and if $dI(x)$ represents the loss of intensity in traversing an additional distance dx then the total number of interactions (per unit time) in the volume element $A\,dx$ will be given by

$$-A\,dI(x) = \sigma\,I(x)\,(NAdx) \tag{10}$$

where σ represents the total cross-section [see Eq. (3)]*, the quantity $(NAdx)$ represents the number of scatterers in the volume element Adx and the negative sign is due to the fact that $I(x)$ decreases with x; we have neglected multiple scatterings in the volume element $A\,dx$. Simple integration of Eq. (10) gives

$$I(x) = I_0 e^{-\Sigma x} \tag{11}$$

where $\Sigma = N\sigma$ is known as the macroscopic cross-section and can be interpreted as the inverse of the mean free path. Further, it can be easily seen that the probability that the particle undergoes its first scattering between x and $x + dx$ will simply be given by

$$p(x)\,dx = e^{-\Sigma x}\,\Sigma\,dx$$

where the factor $e^{-\Sigma x}$ represents the probability that it does not undergo

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*We are assuming here that the number of particles scattered is simply the sum of the numbers scattered by each atom. In the quantum theory, we will see that if different atoms of the target act coherently, then we cannot simply add scattering cross-sections as above since interference effects are involved. One then has to add the scattering probability *amplitudes* first. An example of this is the scattering of low energy neutrons in crystals (see problems 19.15 and 20.1).

scattering in traversing a distance x and $\Sigma\, dx$ represents the probability that it does undergo scattering in traversing the distance dx. Obviously

$$\int_0^\infty p(x)\, dx = 1$$

as it indeed should be.

19.3 Quantum Theory of Scattering

In quantum mechanics, strictly speaking, the scattering problem needs a temporal description, namely, how a wave packet representing the incident particle as $t \to -\infty$ behaves as it passes through the region of perturbation and proceeds to $t \to \infty$ (See problem 19.19). However, when there is a steady current of particles in the beam, we often dispense with the temporal description. We merely calculate the current of particles at an infinite distance away from the target (as opposed to behaviour at $t \to \infty$). This is done by looking for asymptotic solutions of the time-independent Schrödinger equation. Since in this region the particles are free, we are dealing with the continuous spectrum of positive energies.

We start with the time independent Schrödinger equation

$$\nabla^2 \psi(\mathbf{r}) + \frac{2\mu}{\hbar^2}[E - V(\mathbf{r})]\psi(\mathbf{r}) = 0 \tag{12}$$

where, if we are considering a fixed scattering centre, μ represents the mass of the particle. On the other hand, if we are considering a two-body interaction then μ represents the reduced mass of the system provided the potential energy function depends only on the magnitude of the distance between the two particles, i.e., $V = V(|\mathbf{r}_1 - \mathbf{r}_2|)$; such potentials are known as spherically symmetric potentials, examples of which are the square well potential [see Eq. (79)], the Coulomb potential (see Sec. 5.3), the exponential potential (see Problem 5.7), etc. Then E [in Eq. (12)] represents the energy in the centre of mass system and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ represents the relative co-ordinate (see Secs. 5.3 and 19.8). The cross-section is calculated in the centre of mass system and the relation which enables one to calculate the cross-section in the laboratory system is discussed in Sec. 19.8.

In order to describe the scattering experiment we will obtain the solution of the Schrödinger equation [Eq. (12)] in the form of an incident plane wave and an outgoing scattered wave. Thus we seek a solution of the form:

$$\psi(r) \underset{r\to\infty}{\to} e^{i\mathbf{k}\cdot\mathbf{r}} + f(\theta)\frac{e^{ikr}}{r} \tag{13}$$

where $\mathbf{k} = k\,\hat{\mathbf{z}}$, $\hat{\mathbf{z}}$ representing a unit vector along the z-axis. We may mention here that for a short range force [i.e., when $\underset{r\to\infty}{\mathrm{Lt}}\, rV(r) = 0$] the general form of the asymptotic solution of Schrödinger equation will be of the form (see Appendix O)

$$f(\theta)\,\frac{e^{ikr}}{r} + g(\theta)\,\frac{e^{-ikr}}{r} \tag{14}$$

where the second term corresponds to an incoming wave and hence neglected in Eq. (13). It may be noted that since the potential is assumed to be spherically symmetric, the amplitude of the scattered wave (i.e., the function f) is assumed to be independent of the azimuthal angle φ.

If we multiply Eq. (13) by the appropriate time factor $\exp(-iEt/\hbar)$, it will be seen that the first term represents a plane wave propagating along the z-axis. Since $|e^{ikz}|^2 = 1$ the number of particles crossing an unit area per unit time is simply

$$v_\infty = \frac{\hbar k}{m} \tag{15}$$

[see Eqs. (38) and (40) of Chapter 2]. Corresponding to the second term in Eq. (13) the current density is given by [see Eq. (36) of Chapter 2 and also Problem 2.4]

$$\mathbf{J} = \mathrm{Re}\left[\frac{e^{-ikr}}{r} f^*(\theta)\,\frac{\hbar}{im}\,\nabla\left(\frac{e^{ikr}}{r}\,f(\theta)\right)\right] \tag{16}$$

or $$\mathbf{J} \simeq v_\infty\,\frac{|f(\theta)|^2}{r^2}\,\hat{\mathbf{r}} \tag{17}$$

where we have neglected terms of $O(1/r^3)$ which will make a negligible contribution at large values of r. The $1/r^2$ dependence of $\mathbf{J}$ implies that the intensity of the scattered wave falls off according to the inverse square law (see Problem 2.4). The function $f(\theta)$ describes the angular distribution of the scattered wave and is known as the *scattering amplitude*. It should be pointed out that in our analysis we have calculated the current density due to the two parts of the wavefunction separately. This is justified because in an actual experiment the incident wave is collimated and does not interfere with the scattered wave.

Now, in Fig. 19.1 the area dA is given by

$$dA = r^2 d\Omega \tag{18}$$

Therefore, the number of particles scattered in the solid angle $d\Omega$ will be equal to the number that crosses the area dA and hence equal to

$$\frac{v_\infty}{r^2}\,|f(\theta)|^2\,r^2 d\Omega \tag{19}$$

Thus*

$$\sigma(\theta) = \left[\frac{d\sigma}{d\Omega}\right] = |f(\theta)|^2 \tag{20}$$

---

*In general, the scattering amplitude f depends on θ and φ; but for spherically symmetric potentials, the scattering amplitude and therefore σ is independent of the azimuthal angle.

Notice that multiplication of the RHS of Eq. (13) by an arbitrary constant would not have changed $\sigma(\theta)$.

In order to obtain a solution of Eq. (12) of the form of Eq. (13), we rewrite Eq. (12) in the form

$$(\nabla^2 + k^2)\,\psi(\mathbf{r}) = F(\mathbf{r}) \tag{21}$$

where

$$k^2 = 2\mu E/\hbar^2 \qquad \text{and} \quad F(\mathbf{r}) = \frac{2\mu}{\hbar^2} V(\mathbf{r})\,\psi(\mathbf{r})$$

We consider Eq. (21) as an inhomogeneous equation and write the soultion in the form

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) + v(\mathbf{r}) \tag{22}$$

where $\phi(\mathbf{r})$ is a solution of the homogeneous equation

$$(\nabla^2 + k^2)\,\phi(\mathbf{r}) = 0 \tag{23}$$

For the scattering problem in which the incident beam travels along k, we choose

$$\phi(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{24}$$

Let $A(\mathbf{k}')$ be the Fourier transform of $v(\mathbf{r})$ [we use $\mathbf{k}'$ and not $\mathbf{k}$ so that the Fourier transform variable does not get confused with k^2 in Eq. 21]; i.e.,

$$A(\mathbf{k}') = \frac{1}{(2\pi)^{3/2}} \int v(\mathbf{r})\, e^{-i\mathbf{k}'\cdot\mathbf{r}}\, d\mathbf{r} \tag{25}$$

Taking the inverse Fourier transform (see Appendix D)

Thus $$v(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \int A(\mathbf{k}')\, e^{i\mathbf{k}'\cdot\mathbf{r}}\, d\mathbf{k}' \tag{26}$$

$$\begin{aligned}
F(\mathbf{r}) &= (\nabla^2 + k^2)\,\psi(\mathbf{r}) = (\nabla^2 + k^2)\,v(\mathbf{r}) \\
&= \frac{1}{(2\pi)^{3/2}} (\nabla^2 + k^2) \int A(\mathbf{k}')\, e^{i\mathbf{k}'\cdot\mathbf{r}}\, d\mathbf{k}' \\
&= \frac{1}{(2\pi)^{3/2}} \int A(\mathbf{k}')\,(k^2 - k'^2)\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{k}' \\
&= \frac{1}{(2\pi)^{3/2}} \int B(\mathbf{k}')\, e^{i\mathbf{k}'\cdot\mathbf{r}}\, d\mathbf{k}'
\end{aligned}$$

where we have operated ∇^2 inside the integral and $B(\mathbf{k}') \equiv A(\mathbf{k}')\,(k^2 - k'^2)$. The above equation tells us that $F(\mathbf{r})$ is the Fourier transform of $B(\mathbf{k}')$ and therefore taking the inverse Fourier transform (see Appendix D) we get

$$A(\mathbf{k}')\,(k^2 - k'^2) = B(\mathbf{k}') = \frac{1}{(2\pi)^{3/2}} \int F(\mathbf{r})\, e^{-i\mathbf{k}'\cdot\mathbf{r}}\, d\mathbf{r} \tag{27}$$

Substituting for $A(\mathbf{k}')$ from Eq. (27) in Eq. (26), we get [we replace $\mathbf{r}$ by $\mathbf{r}'$ in Eq. (27) so that it does not get confused with $\mathbf{r}$ in Eq. (26)]:

$$v(\mathbf{r}) = -\frac{1}{8\pi^3}\int\int \frac{1}{(k'^2-k^2)} F(\mathbf{r}') \exp\left[i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')\right] d\mathbf{r}'\, d\mathbf{k}'$$

which can be written in the form

$$v(\mathbf{r}) = \int G(\mathbf{r},\mathbf{r}')\, F(\mathbf{r}')\, d\mathbf{r}' \tag{28}$$

where

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{8\pi^3}\int \frac{1}{(k'^2-k^2)} \exp\left[i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')\right] d\mathbf{k}' \tag{29}$$

is known as the Green's function* for the operator (∇^2+k^2). We define a new variable $\boldsymbol{\rho} = \mathbf{r}-\mathbf{r}'$ and choose the direction of the polar axis (i.e., the direction of k'_z) along $\boldsymbol{\rho}$ to get $\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}') = \mathbf{k}'\cdot\boldsymbol{\rho} = k'\rho\cos\theta$ so that

$$G(\rho) = -\frac{1}{8\pi^3}\int_0^\infty \frac{k'^2\,dk'}{k'^2-k^2}\int_0^\pi e^{ik'\rho\cos\theta}\sin\theta\, d\theta\int_0^{2\pi} d\varphi$$

$$= -\frac{1}{8\pi^3}\cdot 2\pi\int_0^\infty \frac{k'^2\,dk'}{k'^2-k^2}\left[\frac{e^{ik'\rho}-e^{-ik'\rho}}{ik'\rho}\right]$$

$$= -\frac{1}{4\pi^2 i\rho}\int_{-\infty}^{+\infty} dk'\left[\frac{k' e^{ik'\rho}}{(k'+k)(k'-k)}\right]$$

We integrate this by going over to the complex k'-plane. The integrand has poles on the real axis at $k' = \pm k$. For the contour we shall choose the real axis

---

*The Green's function is actually defined through the equation

$$(\nabla^2+k^2)\, G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$$

where $\delta(\mathbf{r}-\mathbf{r}')$ is the 3-dimensional Dirac delta function (see Appendix F). In terms of the Green's function, the solution of Eq. (21) is

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) + \int G(\mathbf{r},\mathbf{r}')\, F(\mathbf{r}')\, d\mathbf{r}'$$

One can check that the above equation solves Eq. (21) by direct substitution

$$(\nabla^2+k^2)\psi = (\nabla^2+k^2)\phi + \int(\nabla^2+k^2)\, G(\mathbf{r},\mathbf{r}')\, F(\mathbf{r}')\, d\mathbf{r}'$$

$$= \int \delta(\mathbf{r}-\mathbf{r}')\, F(\mathbf{r}')\, d\mathbf{r}' = F(\mathbf{r})$$

where we have used Eq. (23). Appendix P gives a slightly different approach for evaluating the Green's function.

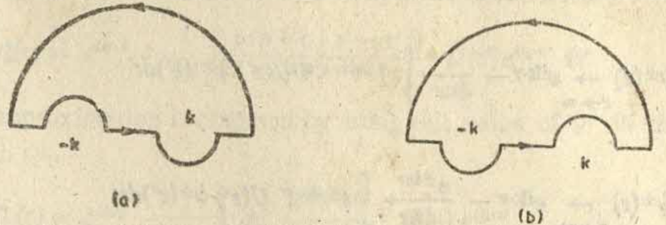

Fig. 19.4 The two contours of integration chosen

closed by the infinitely far upper half semicircle (see Fig. 19.4) since the factor $e^{ik'\rho}$ ensures that the integral vanishes on the upper half semicircle; this follows from Jordan's lemma (see, for example, Pipes, 1958).

There, however, remains the important question of how to go around the two poles. We shall choose the two contours shown in Figs. 19.4(a) and (b). In case (a), the result is

$$G(\rho) = -\frac{1}{4\pi^2\rho i}\,2\pi i\left[\frac{k'e^{ik'\rho}}{k'+k}\right]_{k'=k} \tag{30}$$

This gives

$$G_+(\rho) = -\frac{e^{ik\rho}}{4\pi\rho} \tag{31a}$$

Similarly case (b) gives

$$G_-(\rho) = -\frac{e^{-ik\rho}}{4\pi\rho} \tag{31b}$$

Another way of formulating the rules for evaluating $G_\pm$ is that for G_+ we replace k in the denominator in the integral in Eq. (30) by $k+i\epsilon$ and for G_- we replace k by $k-i\epsilon$ always remembering that ϵ is positive and letting $\epsilon \to 0$.

We can now write down the corresponding solutions for ψ from Eq. (24),

$$\psi^\pm(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi}\int\frac{\exp(\pm ik\,|\,\mathbf{r}-\mathbf{r}'\,|)}{|\,\mathbf{r}-\mathbf{r}'\,|}\,U(\mathbf{r}')\,\psi^\pm(\mathbf{r}')\,d\mathbf{r}' \tag{32}$$

We make two remarks about these solutions. First, any linear combination of ψ^+ and ψ^- will also be a solution. Secondly, we really have not solved anything since Eq. (32) is an integral equation with the unknown $\psi^\pm$ appearing on both sides. Actually we need the asymptotic forms, i.e., the form of $\psi(\mathbf{r})$ for $\mathbf{r} \to \infty$. If we assume that $U(\mathbf{r}') \neq 0$ only for a finite region, say $|\,\mathbf{r}'\,| < a$ then for $r \to \infty$, the main contribution of the integral in Eq. (32) comes from a region where $r' \ll r$; thus we may write

$$|\,\mathbf{r}-\mathbf{r}'\,| = r\left[1-\frac{2\mathbf{r}\cdot\mathbf{r}'}{r^2}+\frac{r'^2}{r^2}\right]^{\frac{1}{2}} \approx r-\mathbf{r}\cdot\mathbf{r}' \tag{33}$$

so that*

$$\psi^{\pm}(\mathbf{r}) \underset{r\to\infty}{\to} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi r}\int e^{\pm ik(r-\hat{\mathbf{r}}\cdot\mathbf{r}')}U(\mathbf{r}')\,\psi^{\pm}(\mathbf{r}')d\mathbf{r}' \tag{34}$$

or,

$$\psi^{\pm}(\mathbf{r}) \underset{r\to\infty}{\to} e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{e^{\pm ikr}}{4\pi r}\int e^{\pm i\mathbf{k}'\cdot\mathbf{r}'}\,U(\mathbf{r}')\,\psi^{\pm}(\mathbf{r}')d\mathbf{r}' \tag{35}$$

where $\mathbf{k}' \equiv k\hat{\mathbf{r}}$ is a vector along the direction of scattering. Equation (35) is of the form

$$\psi^{\pm}(\mathbf{r}) \to e^{i\mathbf{k}\cdot\mathbf{r}} + f_k(\theta, \varphi)\,\frac{e^{\pm ikr}}{r} \tag{36}$$

where θ, φ are the polar angles of the scattered particle.

We recall that for the complete solutions we must multiply Eq. (36) by the time part, $\exp(-i\omega t)$, where k and ω are related by the free particle equation

$$\frac{\hbar^2 k^2}{2\mu} = \hbar\omega$$

We now recognize that $\psi^+(\mathbf{r})$ represents a plane wave term plus an outgoing wave while $\psi^-(\mathbf{r})$ represents a plane wave plus an incoming wave. We now restrict ourselves to the solution corresponding to the outgoing wave case $\psi^+(\mathbf{r})$. The term

$$f_k(\theta, \varphi) = -\frac{1}{4\pi}\int \exp(-i\mathbf{k}'\cdot\mathbf{r}')\,U(\mathbf{r}')\,\psi^+(\mathbf{r}')d\mathbf{r}' \tag{37}$$

is called the *scattering amplitude*. Generally in scattering experiments the detector is placed outside the region of the incident beam and counts only the scattered part. It can be seen that the amplitude of the scattered beam decreases as $1/r$ implying that the intensity decreases as $1/r^2$ as it indeed should be. Once $f(\theta, \varphi)$ is known, the scattering cross-section can be calculated using the relation

$$\frac{d\sigma}{d\Omega} = |f(\theta, \varphi)|^2 \tag{38}$$

19.4 The Born Approximation

The scattering amplitude [Eq. (37)] cannot be evaluated unless we know $\psi^+(\mathbf{r}')$ in the first place. However, if the interaction energy U is treated as a small

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*In writing Eq. (34) we have replaced $|\mathbf{r} - \mathbf{r}'|$ by r in the denominator because

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} \simeq \frac{1}{r} + \frac{1}{r^2}\,\hat{\mathbf{r}}\cdot\mathbf{r}' + \ldots.$$

implying that the second term would have led to a term $O(1/r^2)$.

perturbation, then we can solve for ψ^+ by the method of successive approximations. From Eq. (32) we obtain as the first approximation [setting $\psi^+(\mathbf{r}') = e^{i\mathbf{k}\cdot\mathbf{r}'}$]

$$\psi_1^+(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi}\int \frac{\exp(ik\mid\mathbf{r}-\mathbf{r}'\mid)}{\mid\mathbf{r}-\mathbf{r}'\mid} U(\mathbf{r}')e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\mathbf{r}' \tag{39}$$

The next approximation is obtained by using this value of ψ^+ in the integral in Eq. (32), i.e.,

$$\begin{aligned}\psi_2^+(\mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi}\int d\mathbf{r}'\,\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\,U(\mathbf{r}')\,e^{i\mathbf{k}\cdot\mathbf{r}'}\\ &\quad + \left(\frac{1}{4\pi}\right)^2\iint d\mathbf{r}'\,d\mathbf{r}''\,\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\,U(\mathbf{r}')\,\frac{e^{ik|\mathbf{r}'-\mathbf{r}''|}}{|\mathbf{r}'-\mathbf{r}''|}\,U(\mathbf{r}'')\,e^{i\mathbf{k}\cdot\mathbf{r}''}\end{aligned} \tag{40}$$

The term $\psi_n^+(\mathbf{r})$ obtained by this procedure is called the *nth Born approximation.* Frequently, one uses only the first term and it is referred to as *the* Born approximation. The first Born approximation for the scattering amplitude is obtained by setting $\psi^+(\mathbf{r}') = \exp(i\mathbf{k}\cdot\mathbf{r}')$ in Eq. (37)

$$\begin{aligned}f_B(\theta,\varphi) &= -\frac{1}{4\pi}\int e^{-i\mathbf{k}'\cdot\mathbf{r}'}\,U(\mathbf{r}')\,e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\mathbf{r}'\\ &= -\frac{1}{4\pi}\int U(\mathbf{r}')\,e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}'}\,d\mathbf{r}'\end{aligned}$$

Inserting the expression for U in terms of V,

$$f(\theta,\varphi) = -\frac{\mu}{2\pi\hbar^2}\int V(\mathbf{r}')e^{-i\mathbf{q}\cdot\mathbf{r}'}\,d\mathbf{r}' \tag{41}$$

where $\hbar\mathbf{q} = \hbar(\mathbf{k}'-\mathbf{k})$ is the momentum transfer in scattering. We may also write

$$f(\theta,\varphi) = -\frac{\mu}{2\pi\hbar^2}V_{\mathbf{q}} \tag{42}$$

where

$$V_{\mathbf{q}} = \int V(\mathbf{r})\,e^{-i\mathbf{q}\cdot\mathbf{r}}\,d\mathbf{r} \tag{43}$$

is the Fourier transform of the potential. For spherically symmetric potentials

$$V(\mathbf{r}') = V(r'), \tag{44}$$

and one obtains

$$f(\theta,\varphi) = -\frac{\mu}{2\pi\hbar^2}\iiint \pi'^2\,dr'\sin\theta'\,d\theta'\,d\varphi'\,V(r')\,e^{-iqr'\cos\theta'}$$

where we have assumed the z'-axis to be along $\mathbf{q}$, and

$$q = |\,\mathbf{k}'-\mathbf{k}\,| = 2k\sin\frac{\theta}{2} \tag{45}$$

θ being the angle of scattering (the angle between $\mathbf{k}'$ and $\mathbf{k}$). Carrying out the integrations we get

$$f(\theta) = -\frac{2\mu}{\hbar^2}\int_0^\infty V(r')\,\frac{\sin qr'}{qr'}\,r'^2\,dr' \tag{46}$$

and

$$\sigma(\theta) = \left(\frac{2\mu}{\hbar^2}\right)^2 \left|\int_0^\infty V(r')\,\frac{\sin qr'}{qr'}\,r'^2\,dr'\right|^2 \tag{47}$$

Suppose now $V(\mathbf{r}')$ is a potential which has the same sign everywhere. Then Eq. (41) shows that for large values of q there will be large phase differences from different regions of the scatterer (i.e., the exponential term oscillates) and effects from different regions will tend to reduce the scattering amplitude. On the other hand for $q = 0$ (i.e., $\mathbf{k}'$ parallel to $\mathbf{k}$) the amplitude will be the largest. The scattering amplitude in this case is

$$f(0) = -\frac{\mu}{2\pi\hbar^2}\int V(\mathbf{r}')\,d\mathbf{r}' \tag{48}$$

The ratio $f(\mathbf{q})/f(0)$ is called *the form factor*. Another way of looking at the problem is to study the difference between a 'point' scatterer and a 'spread out' one. It is easy to see that, in general, the effect of a spread is to reduce the scattering.

The Born approximation is useful when the scattered wave is negligible compared to the incident wave. Looking at Eq. (39) this implies that

$$\left|\frac{1}{4\pi}\int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\,U(\mathbf{r}')\,e^{i\mathbf{k}\cdot\mathbf{r}'}\,d\mathbf{r}'\right| \ll 1 \tag{49}$$

For short range central potentials, we can put $r \approx 0$ and obtain a crude limit

$$\frac{2\mu}{\hbar^2 k}\left|\int_0^\infty e^{ikr'}\sin kr'\,V(r')\,dr'\right| \ll 1 \tag{50}$$

a result that is likely to hold for weak potentials and high energies.

19.4.1 APPLICATION OF BORN APPROXIMATION FOR THE SHIELDED COULOMB POTENTIAL

As an example we consider the shielded Coulomb potential for which the potential energy function is given by (see, e.g., Reitz and Milford, 1960, Sec. 14-1)*

$$V(r) = \frac{Z_1 Z_2\, e^2}{r}\exp\left(-\frac{r}{\lambda}\right) \tag{51}$$

---

*We are, for the sake of convenience, using the CGS units. In MKS units e^2 should be replaced by $q^2/4\pi\epsilon_0$ but then there would be confusion between the charge q and the momentum transfer vector $\hbar\mathbf{q}$.

where λ is known as the shielding distance. Substituting in Eq. (46) we get

$$\sigma(\theta) = \frac{4\mu^2}{\hbar^4 q^2}\left(Z_1 Z_2 e^2 \right)^2 \left| \int_0^\infty e^{-r/\lambda} \sin qr \, dr \right|^2$$

The integral is the imaginary part of $\int_0^\infty e^{-r/\lambda} e^{iqr}\, dr$ and gives

$$\frac{q}{q^2 + 1/\lambda^2}$$

Thus

$$\sigma(\theta) = \frac{4\mu^2 (Z_1 Z_2 e^2)^2}{\hbar^4 (q^2 + 1/\lambda^2)^2} = \frac{4\mu^2 (Z_1 Z_2 e^2)^2}{\left(4 p^2 \sin^2\frac{\theta}{2} + \frac{\hbar^2}{\lambda^2}\right)^2} \tag{52}$$

If we let $\lambda \to \infty$, we get

$$\sigma = \frac{(Z_1 Z_2 e^2)^2}{16 E^2 \sin^4\frac{\theta}{2}} \tag{53}$$

which is exactly the same as obtained using classical mechanics (see Problem 19.22). Indeed even the exact analysis (see Sec. 19.6) gives the same result.

19.5 The Method of Partial Waves

In the previous section we have discussed the Born approximation and have also given approximate conditions for its validity. When the Born approximation fails, it is necessary to use other methods; one such method is the method of partial waves which is applicable to spherically symmetric potentials. For such a potential, the angular momentum of the scattered particle is a constant of motion. It is therefore advantageous to develop solutions in terms of angular momentum eigenfunctions. If the potential is of sufficiently short range (or the energy of the incident particles is low), it will turn out that only a few eigenfunctions with small angular momenta (that is, only a few partial waves) will really be affected by the potential. Assuming that the incident momentum is $\hbar k$, large angular momenta correspond roughly to large values of the impact parameter* and hence the particle is hardly deflected. If the range of the potential is a it usually suffices to consider angular momenta $l\hbar$ with

$$l \leqslant ka \tag{54}$$

We assume that particles of momenta $\hbar k$ are incident along the z-direction. The plane wave representing the incident particle can be expanded in terms of angular momentum eigenfunctions (j_l are spherical Bessel functions in the following)

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*Classically the angular momentum of the particle is $mv_0 s$ (see Fig. 19.2) and clearly for $s > a$ (where a is the range of the potential) there is no scattering of the particle.

$$\exp(i\mathbf{k}\cdot\mathbf{r}) = e^{ikz} = \sum_{l=0}^{\infty} i^l (2l+1) P_l(\cos\theta)\, j_l(kr) \tag{55}$$

where there is no azimuthal angular dependence in the expansion due to symmetry around the z-axis [see Appendix N for the derivation of Eq. (55)]. It is clear that the scattering amplitude must also be independent of φ since the potential, being spherically symmetric, does nothing to discriminate between various values of φ. For large $\mathbf{r}$ the asymptotic form of j_l is (see Appendix H)

$$\begin{aligned} j_l(kr) &\underset{r\to\infty}{\to} \frac{\sin(kr - l\pi/2)}{kr} \\ &\underset{r\to\infty}{\to} \frac{\exp[i(kr - l\pi/2)] - \exp[-i(kr - l\pi/2)]}{2ikr} \end{aligned} \tag{56}$$

With the insertion of the time factor $\exp(-i\omega t)$, it is clear from Eqs. (55) and (56) that the plane wave contains equal amplitudes of incoming and outgoing spherical waves. Thus the asymptotic form of Eq. (55) will be

$$e^{ikz} = e^{ikr\cos\theta} \to \sum_l \frac{(2l+1)}{2ikr}\left[e^{ikr} - (-1)^l e^{-ikr}\right] P_l(\cos\theta) \tag{57}$$

Now, the Schrödinger equation for the problem is, as before, $(\nabla^2 + k^2)\psi = U\psi$. We now expand $\psi(\mathbf{r})$ in the form

$$\psi(\mathbf{r}) = \sum_l \frac{(2l+1)}{k}\, i^l\, \frac{u_l(r)}{r} P_l(\cos\theta) \tag{58}$$

In writing down Eq. (58), we make the following observations:

(*a*) Since, in the Schrödinger equation, Eq. (21), the potential is spherically symmetric, the spherical harmonics $Y_{lm}(\theta, \varphi)$ are solutions (see Sec. 5.2); in this problem $m = 0$, there being no φ-dependence. We can, therefore, take the general solution to be a linear combination of Y_{l0} or $P_l(\cos\theta)$.

(*b*) The factors $(2l+1)\, i^l/k$ are introduced for convenience. Clearly, for Eq. (58) to be correct, $u_l(r)$ must solve the Schrödinger equation, Eq. (21).

Substituting Eq. (58) into Eq. (21) we obtain

$$\frac{d^2u_l}{dr^2} + \left[k^2 - U(r) - \frac{l(l+1)}{r^2}\right] u_l(r) = 0 \tag{59}$$

In Appendix O, we have shown that for a short range force for which

$$\lim_{r\to\infty} r\,V(r) = 0 \tag{60}$$

the asymptotic form of $u_l(r)$ will be exp $(\pm ikr)$; thus we may write*

$$u_l(r) \xrightarrow[r\to\infty]{} A_l e^{ikr} + B_l e^{-ikr} = C_l \sin\left(kr - \frac{l\pi}{2} + \delta_l\right) \tag{61}$$

where the factor $l\pi/2$ has been introduced for the sake of convenience and the quantities δ_l are known as phase shifts**. Equation (61) can be written in the form

$$u_l \sim \frac{1}{2i} C_l(-i)^l [e^{i\delta_l} e^{ikr} - (-1)^l e^{-i\delta_l} e^{-ikr}] \tag{62}$$

Substituting Eq. (62) into Eq. (58), we obtain

$$\psi(\mathbf{r}) \underset{\text{large } r}{\to} \sum_l \frac{(2l+1)}{2ikr} C_l [e^{i\delta_l} e^{ikr} - (-1)^l e^{-i\delta_l} e^{-ikr}] P_l(\cos\theta) \tag{63}$$

This is to be compared with the form

$$\begin{aligned}\psi(\mathbf{r}) &\to e^{ikz} + \frac{e^{ikr}}{r} f(\theta)\\ &= \sum_l \frac{(2l+1)}{2ikr} P_l \left[e^{ikr} - (-1)^l e^{-ikr} \right] + \frac{e^{ikr}}{r} f(\theta)\end{aligned} \tag{64}$$

where we have used Eq. (57). Equations (63) and (64) represent the same function and hence the coefficients of exp (ikr) and exp $(-ikr)$ should be identical; equating the coefficients gives us

$$C_l = e^{i\delta_l}$$

and

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1) \frac{\exp(2i\delta_l) - 1}{2ik} P_l(\cos\theta) \tag{65}$$

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*This may be very easily seen for a potential which vanishes beyond a certain distance $r = a$; because then for $r > a$, $R_l(r)$ $(= u_l(r)/r)$ satisfies the equation satisfied by spherical Bessel functions and therefore [see Eqs. (14) and (15) of Appendix H]

$$u_l(r) \xrightarrow[r\to\infty]{} \rho\,[a_l\, j_l(\rho) + b_l\, n_l(\rho)]$$

where $\rho = kr$ and j_l and n_l are the spherical Bessel and spherical Neumann functions (see Appendix H). Using the asymptotic forms of j_l and n_l (see Appendix H) we get

$$u_l(\rho) \xrightarrow[r\to\infty]{} \left[a_l \frac{1}{\rho} \sin\left(\rho - \frac{l\pi}{2}\right) + b_l \cos\left(\rho - \frac{l\pi}{2}\right)\right]$$

which is identical in form to Eq. (61) with $\delta_l = \tan^{-1}(b_l/a_l)$.

**When $V(r) = 0$ everywhere, $u_l(r)$ is simply $krj_l(kr)$ [see Eq. (55)] the asymptotic form of which is $\sin(kr - l\pi/2)$. Thus δ_l is the 'phase shift' introduced by the potential.

or

$$f(\theta) = \sum_{l=0}^{\infty} \frac{(2l+1)}{k} \sin \delta_l \exp(i\delta_l)\, P_l(\cos\theta) \tag{66}$$

The total cross-section can be shown to be (see Problem 19.16)

$$\sigma = \int |f(\theta)|^2\, d\Omega = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2\delta_l \tag{67}$$

The above expression shows that as far as the total cross-section is concerned, the different partial waves contribute independently, there being no interference. This, however, is not the case for the differential cross-section.

As an application of the method of partial waves, we will consider two examples.

19.5.1 SCATTERING BY A HARD SPHERE

We first consider the scattering by a hard sphere for which $V(r)$ will be given by

$$\begin{aligned} V(r) &= 0 && r > a \\ &= \infty && r < a \end{aligned} \tag{68}$$

Since the region $r < a$ is inpenetrable, the wavefunction must vanish at $r = a$. Now, for $r > a$ the radial part of the Schrödinger equation is [see Eq. (21)]

$$\frac{d^2u_l}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2} \right] u_l(r) = 0 \tag{69}$$

For $l = 0$, the solution (which vanishes at $r = a$) is given by

$$u_0(r) = A \sin k(r-a) \tag{70}$$

Comparing with Eq. (61) we get

$$\delta_0 = -ka \tag{71}$$

which is known as the *s*-wave (or $l = 0$) phase shift. In general, (for arbitrary l) the solution is (see Appendix H)

$$u_l(r) = (kr)\,[A_l j_l(kr) + B_l n_l(kr)] \qquad \text{for} \quad r > a \tag{72}$$

Using the boundary condition at $r = a$ we get

$$\begin{aligned} u_l(r) &= (kr) A_l \left[j_l(kr) - \frac{j_l(ka)}{n_l(ka)} n_l(kr) \right] \\ &\to A_l \left[\sin\left(kr - \frac{l\pi}{2} \right) - \frac{j_l(ka)}{n_l(ka)} \cos\left(kr - \frac{l\pi}{2} \right) \right] \end{aligned} \tag{73}$$

Comparing with Eq. (61) we immediately get

$$\tan \delta_l = -\frac{j_l(ka)}{n_l(ka)}$$

The above equation is an exact result; for $l = 0$, one immeidately gets Eq. (71). For $ka \ll 1$ (i.e., for low energies), if we use Eq. (13) of Appendix H, we would get

$$\tan \delta_l \approx - \frac{(ka)^{2l+1}}{(2l+1)!!\,(2l-1)!!} \tag{75}$$

Since $ka \ll 1$, we get $\delta_1/\delta_0 \ll 1$, $\delta_2/\delta_1 \ll 1$, etc. This result is consistent with our earlier statement that at low energies only few of the angular momenta contribute. Thus for sufficiently low energies, only δ_0 effectively contributes and using Eqs. (67) and (71), we get

$$\sigma \approx \frac{4\pi}{k^2} \sin^2\delta_0 \approx 4\pi a^2 \tag{76}$$

which is four times the result obtained by using classical mechanics (see Problem 19.21). At this point it may be worthwhile to discuss the conditions for the validity of the classical theory in describing the scattering process. The classical theory will be valid when one is justified in describing the scattering through the 'trajectories' of the classical particle. The situation is analogous to the justification of the 'ray-picture' in optics which is valid when the refractive index changes very slowly in distances of the order of wavelength. This is also the condition for the validity of the WKB approximation (see Chapter 13). When diffraction effects become important it is necessary to have a quantum mechanical description of the scattering process.

For the hard sphere case, when $ka \gg 1$

$$\tan \delta_l \approx - \tan\left(ka - \frac{l\pi}{2}\right) \tag{77}$$

so that

$$\begin{aligned} \sigma &\approx \frac{4\pi}{k^2} \sum_{l=0}^{l\approx ka} (2l+1) \sin^2\left(-ka + \frac{l\pi}{2}\right) \\ &\approx \frac{4\pi}{k^2} \int_0^{ka} (2x+1) \sin^2\left(-ka + \frac{x\pi}{2}\right) dx \\ &\approx 2\pi a^2 \end{aligned} \tag{78}$$

which is still a factor of two more than the classical result. This is due to the fact that from the region $\theta \approx 0$ there is a contribution of πa^2; this contribution arises from the famous Poisson diffraction phenomenon according to which when a plane wave is incident normally on an opaque disc, one always obtains a bright spot on the centre of the geometric shadow (for further details one may look up Sommerfeld, 1950, p. 215).

19.5.2 SCATTERING BY A SQUARE WELL AND THE RAMSAUER EFFECT

We next consider the s-wave scattering by a square well

$$\begin{aligned} V(r) &= -V_0 \qquad & 0 < r < a \\ &= 0 & r > a \end{aligned} \tag{79}$$

For $l = 0$, the radial part of the Schrödinger equation would be [see Eq. (59)]

$$\frac{d^2u_0}{dr^2} + K^2u_0(r) = 0 \quad \text{for} \quad 0 < r < a \tag{80}$$

$$\frac{d^2u_0}{dr^2} + k^2u_0(r) = 0 \quad \text{for} \quad r > a \tag{81}$$

where $K^2 = 2m(E + V_0)/\hbar^2$ and $k^2 = 2mE/\hbar^2$. For $r < a$ we must have $u_0 = A \sin Kr$ (the cosine solution will make $R_0(r) = u_0(r)/r$ go to infinity at $r = 0$). For $r > a$ we write the solution in the form $u_0(r) = B \sin(kr + \delta_0)$. Continuity of u and its derivative at $r = a$ gives

$$\tan(ka + \delta_0) = \frac{k}{K} \tan Ka$$

or

$$\delta_0 = \tan^{-1}\left(\frac{k}{K} \tan Ka\right) - ka \tag{82}$$

Thus

$$\sigma \simeq \frac{4\pi}{k^2} \sin^2 \delta_0 = \frac{4\pi}{k^2}\left[1 + \frac{1}{\tan^2 \delta_0}\right]^{-1}$$

$$= 4\pi\left[k^2 + \left(\frac{g + k \tan ka}{1 - g(\tan ka/k)}\right)^2\right]^{-1} \tag{83}$$

where $g = K \cot Ka$.

Returning to Eq. (82) we notice that $\tan \delta_0$ (and hence the scattering cross-section) would vanish if

$$\frac{\tan Ka}{K} = \frac{\tan ka}{k};$$

we are assuming $ka \ll 1$ so that δ_1, δ_2, etc. are negligible. Although the above equation has been derived for a square well potential, similar vanishing of the cross-section would occur for a 'localizable' attractive potential. This effect was first observed by Ramsauer (and hence known as Ramsauer effect) who found that at low energies (~ 0.7 eV) the scattering cross-section of electrons by noble atoms was extremely small. The effect was later explained by quantum theory.

19.5.3 SCATTERING OF NEUTRONS BY PROTONS

The neutron-proton interaction can be approximately described by the square well interaction [see Eq. (79)]. Thus, we may use the results of Sec. 19.5.2 to study the scattering of neutrons by protons. For low energies $ka \to 0$ and Eq. (83) becomes

$$\sigma \approx \frac{4\pi}{k^2 + g^2/(1 - ga)^2} \tag{84}$$

In order to determine the value of g $(= K \cot Ka)$ we use the data on the binding energy for the ground state of deuteron; this is denoted by B and its value is ≈ 2.223 MeV. Now, for the ground state of deuteron $E = -B$ and $l = 0$ so that

$$\begin{aligned} u_0(r) &= A \sin k_1 r \qquad \text{for} \quad r < a \\ &= c\, e^{-\kappa r} \qquad \text{for} \quad r > a \end{aligned}$$

where $\kappa^2 = 2\mu B/\hbar^2$, $k_1^2 = 2\mu(-B + V_0)/\hbar^2$,

$$\mu = \frac{m_n m_p}{m_n + m_p} \approx \frac{1}{2} m_n$$

being the reduced mass of the neutron-proton system. Continuity conditions at $r = a$ give us

$$k_1 \cot k_1 a = -\kappa \tag{85}$$

If $B \ll V_0$ (which is indeed the case because $V_0 \approx 40$ MeV),

$k_1 \approx [2\mu V_0/\hbar^2]^{1/2} \approx K$. Thus

$$g = K \cot Ka \approx k_1 \cot k_1 a = -\kappa = -\left(\frac{2\mu}{\hbar^2} B\right)^{1/2} \tag{86}$$

substituting in Eq. (84) we get

$$\sigma \approx \frac{4\pi}{\dfrac{2\mu E}{\hbar^2} + \dfrac{2\mu B}{\hbar^2 (1 - ga)^2}} \approx \frac{4\pi\hbar^2}{m_n (E + B)} \tag{87}$$

The last step is not very accurate because $ga \sim 0.3$; nevertheless the above expression should give a reasonable estimate for σ. However, if we assume $E \ll B = 2.223$ MeV then the above expression gives $\sigma \approx 2.4 \times 10^{-24}$ cm^2 whereas the experimental value is about 21×10^{-24} cm^2. This large discrepancy cannot be accounted by the approximations made in the analysis. In 1935, Wigner made a suggestion which removed this difficulty. He pointed out that the ground state of deuteron was a triplet; however, there is no reason why neutron and proton could not interact with their spins antiparallel (i.e., through the singlet state). Let E_s denote the energy of the neutron-proton system associated with the singlet state; then

$$\sigma \approx \frac{4\pi\hbar^2}{m_n}\left[\frac{3}{4}\,\frac{1}{E + B} + \frac{1}{4}\,\frac{1}{E + |E_s|}\right] \tag{88}$$

where $\frac{3}{4}$ and $\frac{1}{4}$ are the statistical weights of the triplet and singlet states (see Sec. 15.5). If we assume $|E_s| \approx 40$ KeV we get the right order of magnitude for σ. However, it is not possible to decide whether the state is real or virtual.*

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*Corresponding to the neutron-proton interaction in the triplet state $V_0 \approx 21$ MeV and it is possible to have a bound state ($a \approx 3$ MeV); on the other hand, when the spins are antiparallel $V_0 \approx 12$ MeV and it is not possible to have a bound state. However, for $E \approx 40$ KeV it is possible to have a virtual (or a metastable) state (see Problems 13.16 and 13.17) with a finite lifetime (see, e.g., Bohm, 1951; Bethe and Morrison, 1956; Mott and Massey, 1949).

For low energies ($E \lesssim 4$-5 MeV) the experimental dependence of σ on E is in reasonably good agreement with Eq. (88).

19.5.4 APPOXRIMATE EXPRESSIONS FOR PHASE SHIFTS IN THE BORN APPROXIMATION

In this section we will obtain approximate expressions for the phase shifts when they have small values. We start out with the equations satisfied by $g_l(r)$ [$= kr\, j_l(kr)$] and $u_l(r)$ [see Eqs. (14) and (15) of Appendix H and Eq. (59) of this chapter]:

$$\frac{d^2 g_l}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2}\right] g_l(r) = 0 \tag{89}$$

$$\frac{d^2 u_l}{dr^2} + \left[k^2 - \frac{l(l+1)}{r^2} - U(r)\right] u_l(r) = 0 \tag{90}$$

We multiply Eq. (89) by $u_l(r)$ and Eq. (90) by $g_l(r)$, subtract and integrate to obtain

$$\left[g_l(r)\frac{du_l(r)}{dr} - u_l(r)\frac{dg_l}{dr}\right]_0^r = \int_0^r U(r)\, g_l(r)\, u_l(r)\, dr$$

Both $g_l(r)$ and $u_l(r)$ vanish at $r = 0$; further, we let $r \to \infty$, and use the asymptotic forms [see Eq. (12) of Appendix H and Eq. (61)] to obtain for the left hand side

$$g_l\frac{du_l}{dr} - u_l(r)\frac{dg_l}{dr} \xrightarrow[r\to\infty]{} k\sin\left(kr - \frac{l\pi}{2}\right)\cos\left(kr - \frac{l\pi}{2} + \delta_l\right)$$

$$- k\sin\left(kr - \frac{l\pi}{2} + \delta_l\right)\cos\left(kr - \frac{l\pi}{2}\right) = -k\sin\delta_l$$

Thus

$$\sin\delta_l = -\frac{1}{k}\frac{2\mu}{\hbar^2}\int_0^\infty V(r)\, u_l(r)\, g_l(r)\, dr \tag{91}$$

The above equation is *exact*. Now if the phase shifts are small (which is likely to be valid for high energies or weak potentials) then in carrying out the above integration we may assume

$$u_l(r) \approx g_l(r) = kr\, j_l(kr)$$

Thus

$$\sin\delta_l \approx \delta_l \approx -\frac{2\mu}{k\hbar^2}\int_0^\infty V(r)\,[kr\, j_l(kr)]^2\, dr$$

$$\approx -\frac{\pi\mu}{\hbar^2}\int_0^\infty V(r)\,[J_{l+1/2}(kr)]^2\, r\,dr \tag{92}$$

where use has been made of Eq. (10) of Appendix H. Since Born approximation is also valid under the same conditions, the calculation of δ_l through Eq. (92) is known as the Born approximation. In Table 19.1 we have given the value of δ_0 (for electron scattering by hydrogen—see Problem 19.6) obtained by using the Born approximation (Eq. 92) and have compared with the exact values obtained by numerical solution of the differential equation. Notice that higher the value of k better is the agreement between the two numbers. The agreement with the experimental data is also satisfactory as discussed by Mott and Mossey (1949).

TABLE 19.1*

COMPARISON OF EXACT AND APPARUXIMATE VALUES FOR PHASES

$(a_0 = \hbar^2/\mu e^2)$

ka_0	*Energy* (eV)	δ_0 *Exact*	*Born Approximation*
1.0	13.5	0.905	0.596
2.0	54	0.695	0.602
3.0	122	0.568	0.534
4.0	215	0.490	0.472
5.0	340	0.432	0.422

* Table adapted from Mott and Massey (1949). See also Problem 19.6.

If we use Eq. (92) for δ_l, we should expect $\sigma(\theta)$ to be given by Eq. (47); this is indeed seen from the following

$$f(\theta) = \frac{1}{2ik} \sum_{l=0,1,2\ldots}^{\infty} (2l+1)\, P_l(\cos\theta)\, [\exp(2i\delta_l) - 1] \quad \text{[see Eq. (66)]}$$

$$\simeq \frac{1}{k} \sum_l (2l+1)\, P_l(\cos\theta)\, \delta_l$$

$$\simeq -\frac{1}{k} \sum_l (2l+1)\, P_l(\cos\theta)\, \frac{\pi\mu}{\hbar^2} \int_0^\infty V(r)\, r^2\, [j_l(kr)]^2\, dr$$

(using Eq. 92)

$$\simeq -\frac{2\mu}{\hbar^2} \int_0^\infty \frac{\sin qr}{qr}\, V(r)\, r^2\, dr \tag{93}$$

where $q = 2k \sin \theta/2$ and use has been made of the identity (see, e.g., Watson, 1945),

$$\frac{\sin qr}{qr} = \sum_{l=0,1,2\ldots} (2l + 1)\, P_l(\cos \theta)\, [j_l(kr)]^2 \tag{94}$$

Equation (93) is identical to Eq. (46).

19.6 The Coulomb Scattering

The Coulomb potential

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \tag{95}$$

is such that $\operatorname*{Lt}_{r\to\infty} rV(r)$ does not tend to zero and hence does not describe a short range force (see Appendix O). Thus the results of the previous sections are not applicable. However, the scattering problem corresponding to the Coulomb potential can be solved directly in parabolic co-ordinates, the direction of the beam being an axis of symmetry. The co-ordinate system is

$$x = \sqrt{\xi\eta} \cos \varphi; \;\; y = \sqrt{\xi\eta} \sin \varphi; \;\; z = \tfrac{1}{2} (\xi - \eta) \tag{96}$$

We also have

$$r = \tfrac{1}{2} (\xi + \eta) \tag{97}$$

In terms of the parabolic co-ordinates, the Schrödinger equation [Eq. (12)] for the Coulomb potential becomes

$$-\frac{\hbar^2}{2\mu}\left[\frac{4}{\xi + \eta} \frac{\partial}{\partial \xi}\left(\xi \frac{\partial}{\partial \xi}\right) + \frac{4}{\xi + \eta} \frac{\partial}{\partial \eta}\left(\eta \frac{\partial}{\partial \eta}\right) + \frac{1}{\xi\eta} \frac{\partial^2}{\partial \varphi^2}\right]\psi + \frac{2Z_1 Z_2 e^2}{(\xi + \eta)}\, \psi = E\psi \tag{98}$$

Since we want solutions independent of φ, we write

$$\psi = f_1(\xi)\, f_2(\eta) \tag{99}$$

Substituting from Eq. (99) in Eq. (98), we obtain

$$\frac{1}{f_1} \frac{d}{d\xi}\left(\xi \frac{df_1}{d\xi}\right) + \frac{1}{f_2} \frac{d}{d\eta}\left(\eta \frac{df_2}{d\eta}\right) - \frac{\mu Z_1 Z_2 e^2}{\hbar^2} + \frac{k^2}{4} (\xi + \eta) = 0$$

so that we can separate the equations

$$\frac{d}{d\xi}\left(\xi \frac{df_1}{d\xi}\right) + \left(\frac{1}{4} k^2\xi - \beta_1\right) f_1 = 0 \tag{100a}$$

and

$$\frac{d}{d\eta}\left(\eta \frac{df_2}{d\eta}\right) + \left(\frac{1}{4} k^2\eta - \beta_2\right) f_2 = 0 \tag{100b}$$

with

$$(\beta_1 + \beta_2) = \frac{\mu Z_1 Z_2 e^2}{\hbar^2} \tag{101}$$

The solution we want must be of the form of a plane wave moving along the z-direction plus an outgoing spherical wave. These are proportional to

$$e^{ikz} = e^{ik(\xi-\eta)/2} \tag{102a}$$

and

$$e^{ikr} = e^{ik(\xi+\eta)/2} \tag{102b}$$

Both these forms suggest that we look for a solution of the form

$$e^{ik\xi/2} f_2(\eta)$$

In other words, we choose

$$f_1(\xi) = e^{ik\xi/2} \tag{103}$$

Substituting Eq. (103) into Eq. (100a), we obtain

$$\left(\frac{ik}{2} - \frac{k^2}{4}\xi\right) e^{ik\xi/2} + \left(\frac{1}{4}k^2\xi - \beta_1\right) e^{ik\xi/2} = 0$$

so that

$$\beta_1 = ik/2$$

Substituting this value of β_1 in Eq. (101) we obtain, from Eq. (100b),

$$\frac{d}{d\eta}\left[\eta\,\frac{df_2}{d\eta}\right] + \left[\frac{1}{4}k^2\eta + \left(\frac{ik}{2} - \frac{\mu Z_1 Z_2 e^2}{\hbar^2}\right)\right] f_2 = 0 \tag{104}$$

We try a solution of the form

$$f_2(\eta) = e^{ik\eta/2}\, g(\eta)$$

We have

$$\frac{df_2}{d\eta} = -\frac{ik}{2} e^{-ik\eta/2} g + e^{-ik\eta/2} \frac{dg}{d\eta}$$

$$\frac{d^2 f_2}{d\eta^2} = -\frac{k^2}{4} e^{-ik\eta/2} g - ik\, e^{-ik\eta/2} \frac{dg}{d\eta} + e^{-ik\eta/2} \frac{d^2 g}{d\eta^2}$$

so that Eq. (104) becomes

$$\eta \frac{d^2 g}{d\eta^2} + (1 - ik\eta)\frac{dg}{d\eta} - nkg = 0 \tag{105}$$

where we have written

$$n = \frac{\mu Z_1 Z_2 e^2}{\hbar^2 k} \tag{106}$$

We want to reduce it to the equation satisfied by the confluent hypergeometric function

$$\eta' \frac{d^2g}{d\eta'^2} + (1 - \eta') \frac{dg}{d\eta'} - ag = 0 \tag{107}$$

We identify $ik\eta$ with η', $-in$ with a. Now the solution of Eq. (107) is [see Appendix G]

$$g = {}_1F_1\,(a;\, 1;\, -\eta') = {}_1F_1\,(-in;\, 1;\, ik\eta) \tag{108}$$

For large values of z, the confluent hypergeometric function has the following behaviour [see Appendices G, K and L]

$${}_1F_1\,(a, c, z) = (c - 1)!\left[\frac{(-z)^{-a}}{\Gamma(c - a)} + \frac{Z^{a-c}\, e^z}{\Gamma(a)}\right] \tag{109}$$

Thus the asymptotic form of g can be written as

$$g \sim g_1 + g_2$$

where

$$g_1 = \frac{(-ik\eta)^{in}}{\Gamma(1 + in)} = \frac{[-ik\,(r - z)]^{in}}{\Gamma(1 + in)} \tag{110a}$$

$$g_2 = \frac{(ik\eta)^{-in-1}\, e^{ik\eta}}{\Gamma(-in)} = \frac{[ik(r - z)]^{-in-1}\, e^{ik(r-z)}}{\Gamma(-in)} \tag{110b}$$

Writing

$$\begin{aligned}[-ik(r - z)]^{in} &= e^{in\ln[-ik(r-z)]}\\ &= e^{in\ln[k(r-z)]}\, e^{in\ln(-i)}\end{aligned}$$

Since

$$(-i) = e^{-i\pi/2}$$

this gives

$$e^{in\ln[-i]} = e^{in[-i\pi/2]} = e^{n\pi/2}$$

Thus

$$g_1 = \frac{e^{n\pi/2}\, e^{in\ln[k(r-z)]}}{\Gamma(1 + in)} \tag{111a}$$

Similarly

$$g_2 = \frac{e^{n\pi/2}\, e^{-in\ln[k(r-z)]}\, e^{ik(r-z)}}{ik(r - z)\,\Gamma(-in)} \tag{111b}$$

We recall that the solution required is

$$\psi = e^{ik\xi/2}\, e^{-ik\eta/2}\, g(\eta) \to e^{ikz}\,(g_1 + g_2) \tag{112}$$

From Eqs. (111a), (111b) and (112) it is clear that $e^{ikz} g_1$ gives a modified plane wave and $e^{ikz} g_2$ gives a spherical wave. We can write

$$\psi \to \frac{e^{n\pi/2}}{\Gamma(1+in)} \left\{ \exp\left[in \ln [k(r-z)] + ikz\right] + \frac{\Gamma(1+in)}{\Gamma(-in)} \frac{\exp\left[ikr - in \ln \{k(r-z)\}\right]}{ik(r-z)} \right\} \tag{113}$$

We have

$$\frac{\Gamma(1+in)}{\Gamma(-in)} = \frac{in\,\Gamma(1+in)}{\Gamma(1-in)}$$

We can write

$$\Gamma(1+in) = |\,\Gamma(1+in)\,| \exp(i\sigma_n)$$

Finally

$$\psi \to \frac{e^{n\pi/2}}{\Gamma(1+in)} \left\{ \exp\left[\, ikz + in \ln\{k(r-z)\} \,\right] + \frac{n}{k(r-z)} \exp\left[\, ikr - in \ln k(r-z) + 2i\sigma_n \,\right] \right\} \tag{114}$$

We note that only the phases of the incident and scattered waves are modified. However, the phase of the scattered wave is of the form $-in \ln[k(r-z)] + 2i\sigma_n$ so that it increases indefinitely for large r, although only logarithmically. We can still identify (putting $z = r\cos\theta$)

$$f(\theta) = \frac{n}{k(1-\cos\theta)} \exp\left[-in \ln(1-\cos\theta)\right] \tag{115}$$

as the part containing the angular dependence. This gives the differential cross-section as

$$\frac{d\sigma}{d\Omega} = |\,f(\theta)\,|^2 = \left(\frac{Z_1 Z_2 e^2}{4(\frac{1}{2}\mu v^2)}\right)^2 \frac{1}{\sin^4(\theta/2)} \tag{116}$$

a result that agrees with the classical result (see Problem 19.22) as well as with the Born approximation result (see Eq. 53).

19.7 Considerations for Identical Particles

In this section we will discuss the scattering of identical particles like scattering of protons by protons or of α particles by α particles. However, in order to point out the peculiarities for identical particles we first consider non-identical particles like scattering of protons by α particles. In the centre of mass system the two particles approach each other with the same momentum (see Fig. 19.5 and Sec. 19.8) and after scattering they are again moving in opposite directions. If the detector is such that it could detect either the α particle or the proton then

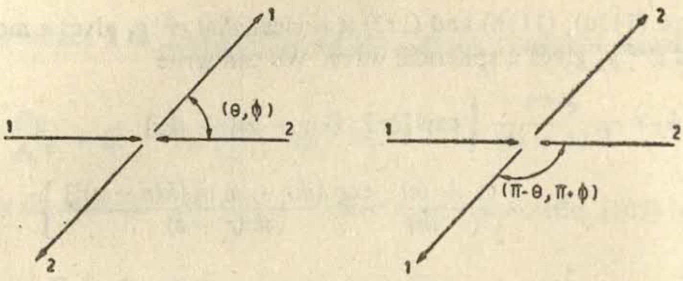

Fig. 19.5 Scattering in the centre of mass system

the detector will register a count if the particle gets scattered along the direction (θ, φ) or along $(\pi - \theta, \pi + \varphi)$ (see Fig. 19.5). Thus the cross-section will be given by

$$\sigma(\theta) = |f(\theta)|^2 + |f(\pi - \theta, \pi + \varphi)|^2 \tag{117}$$

However, since most scattering potentials are spherically symmetric, we get

$$\sigma(\theta) = |f(\theta)|^2 + |f(\pi - \theta)|^2 \tag{118}$$

The above equations give the correct results for non-identical particles like scattering of α particles by protons; however, it gives wrong results for scattering of protons by protons or of alpha particles by alpha particles. This is because of the indistinguishability of identical particles due to which it is impossible to say whether it is the incident particle or the target particle which has reached the detector. Due to this indistinguishability, we must construct appropriate wavefunctions which are either symmetric or antisymmetric with respect to the interchange of indices (see Sec. 15.5).

We first consider identical Fermions (like protons) for which the total wavefunction, space and spin, must be antisymmetric. This means that even the asymptotic form of the wavefunction of a two particle system must obey this rule. However, the space part of the wavefunction alone may be either symmetric or antisymmetric, depending on whether the spin part is antisymmetric or symmetric. Thus for the $p - p$ system, the space wavefunction must be symmetric for the singlet and antisymmetric for the triplet case. In the centre of mass system the collision may be represented as in Fig. 19.5. The asymptotic form of the wavefunction must therefore be a symmetric or an antisymmetric linear combination of the two cases. If

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + f(\theta, \varphi)\frac{e^{ikr}}{r}$$

describes the form for the first, then

$$\psi(-\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}} + f(\pi - \theta, \pi + \varphi)\frac{e^{ikr}}{r} \tag{119}$$

describes the second. The combinations are

$$[\psi(\mathbf{r}) \pm \psi(-\mathbf{r})]$$

The scattering cross-section is now

$$\begin{aligned}\sigma(\theta, \varphi) &= |f(\theta, \varphi) \pm f(\pi - \theta, \varphi + \pi)|^2 \\ &= |f(\theta, \varphi)|^2 + |f(\pi - \theta, \varphi + \pi)|^2 \pm 2\mathrm{Re}[f(\theta, \varphi) f^*(\pi - \theta, \varphi + \pi)]\end{aligned} \tag{120}$$

To check the normalization in Eq. (119), we note that in the absence of interference we get the classical result

$$\sigma(\theta, \varphi) \to |f(\theta, \varphi)|^2 + |f(\pi - \theta, \varphi + \pi)|^2 \tag{121}$$

This result merely says that the detector counting the scattered particles will not be able to say whether it is counting particle 1 or 2 so that the number counted at a particular angle is a sum of both the probabilities.

However, the complete quantum mechanical result, viz. Eq. (120), is more subtle than just this. It is actually the probability amplitudes that interfere. (This situation is quite similar to electron diffraction by the double slit; see Chapter 2).

At $\theta = \pi/2$, for a central potential, the results are particularly interesting. We obtain

$$\sigma\left(\theta = \frac{\pi}{2}\right)_{\text{sym}} = 4\left|f\left(\frac{\pi}{2}\right)\right|^2$$

which is twice the result predicted by the classical equation [Eq. (121)]. Moreover,

$$\sigma\left(\theta = \frac{\pi}{2}\right)_{\text{anti}} = 0$$

Thus the $p - p$ triplet scattering at $\pi/2$ should be absent. For an unpolarized beam of protons, the cross-section is

$$\sigma(\theta) = \tfrac{3}{4}\sigma(\theta)\,|_{\text{triplet}} + \tfrac{1}{4}\sigma(\theta)\,|_{\text{singlet}}$$

because the singlet state has statistical weight one and the triplet state three. Using Eq. (120), we obtain

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 + |f(\pi - \theta)|^2 - \mathrm{Re}[f(\theta) f^*(\pi - \theta)]$$

Equation (115) gives

$$f(\theta) = \frac{n}{2k \sin^2 \theta/2} \exp\left[-in \ln(2 \sin^2 \theta/2)\right]$$

$$f(\pi - \theta) = \frac{n}{2k \cos^2 \theta/2} \exp\left[-in \ln(2 \cos^2 \theta/2)\right]$$

Thus

$$\sigma(\theta) = \frac{n^2}{4k^2}\left\{\frac{1}{\sin^4(\theta/2)} + \frac{1}{\cos^4(\theta/2)} - \frac{\text{Re}\exp[-in\ln(\tan^2(\theta/2)]}{\sin^2(\theta/2)\cos^2(\theta/2)}\right\}$$

$$= \frac{n^2}{4k^2}\left\{\frac{1}{\sin^4(\theta/2)} + \frac{1}{\cos^4(\theta/2)} - \frac{\cos[n\ln(\tan^2(\theta/2))]}{\sin^2(\theta/2)\cos^2(\theta/2)}\right\} \qquad (122)$$

Here $n = \mu Z_1 Z_2 e^2/\hbar^2 k$. This formula agrees with the experimental data at energies which are not large enough so as to let the nuclear interaction become effective. For further details see Roy and Nigam (1967).

It is of interest to mention that for spinless particles (e.g., α particles) the total wavefunction must be symmetric and therefore we must have

$$\sigma(\theta) = |f(\theta) + f(\pi - \theta)|^2 \qquad (123)$$

This equation gives

$$\sigma\left(\theta = \frac{\pi}{2}\right) = 4\left|f\left(\frac{\pi}{2}\right)\right|^2 \qquad (124)$$

which is to be compared with the classical result [Eq. (118)] which gives $\sigma(\theta = \pi/2) = 2.|f(\pi/2)|^2$. Thus the quantum theory predicts twice as much scattering as we would expect from classical theory; the experimental data confirms the quantum result.

19.8 Laboratory and Centre of Mass Co-ordinate Systems

In Sec. 5.3 we had shown that the two body problem can always be reduced to a one body problem provided the potential has spherical symmetry, i.e., the potential energy depended only on the magnitude of the distance between the two particles. It was shown that the Schrödinger equation could be broken up into two one particle equations, one describing the free motion of the centre of mass [see Eq. (31) of Chapter 5] and the other describing the relative motion of the two particles [see Eqs. (27) and (33) of Chapter 5 and Eq. (12) of this chapter]. Thus the cross-sections calculated in this chapter correspond to the centre of mass system and since all measurements are carried out in the laboratory system we must know how to relate the cross-sections in the two systems*. It is the purpose of this section to know the relation between the two systems.

We consider a particle of mass m_1 moving with velocity v_1 towards the target particle of mass m_2 which is initially at rest (see Fig. 19.6a). The centre of mass (shown by C in the figure) moves with velocity

$$v_c = \frac{m_1 v_1}{m_1 + m_2} \qquad (125)$$

After scattering, the incident particle moves in a direction given by the angles

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*It may be mentioned here that while calculating the energies of the bound states in Chapter 5 we could ignore the motion of the centre of mass.

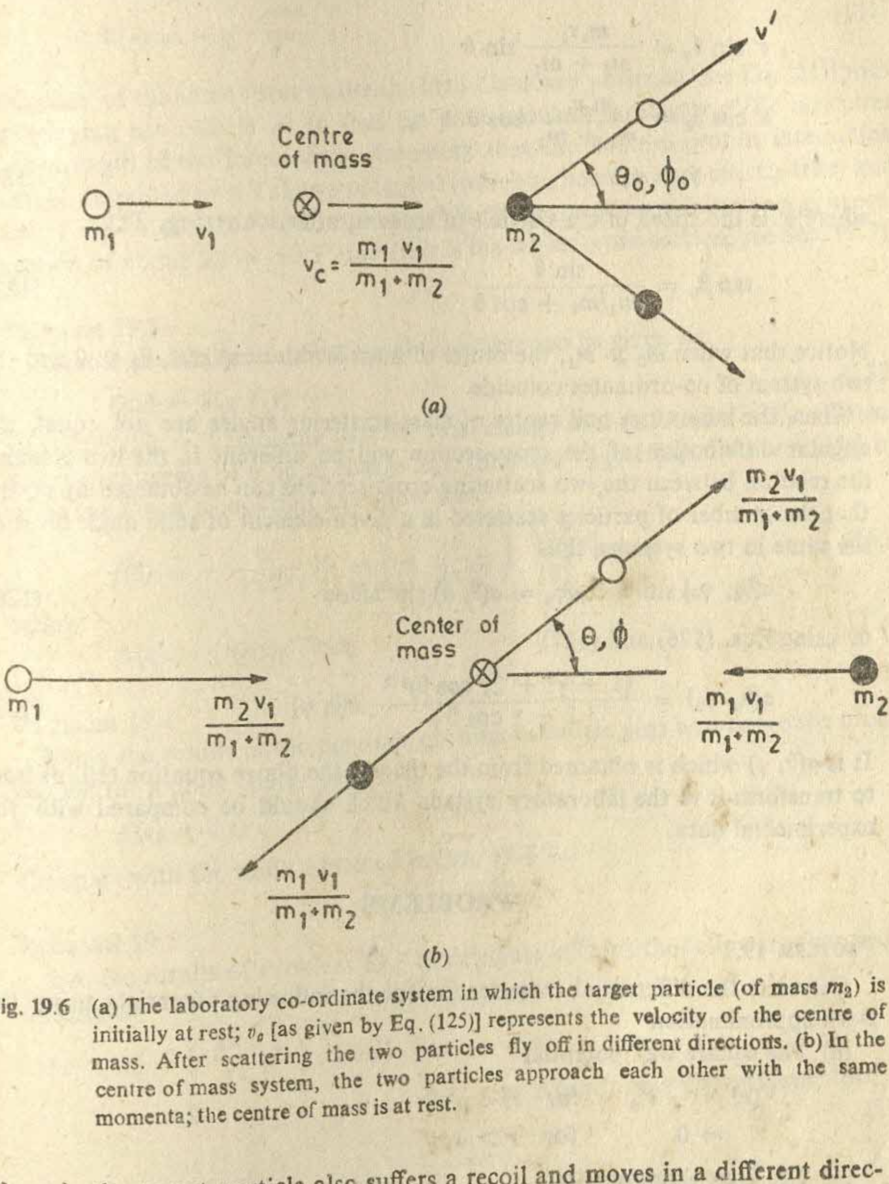
Centre of mass
m_1
v_1
$v_c = \frac{m_1 v_1}{m_1 + m_2}$
m_2
θ_0, ϕ_0
v'
(a)
$\frac{m_2 v_1}{m_1 + m_2}$
Center of mass
θ, ϕ
m_1
$\frac{m_2 v_1}{m_1 + m_2}$
$\frac{m_1 v_1}{m_1 + m_2}$
m_2
$\frac{m_1 v_1}{m_1 + m_2}$
(b)

Fig. 19.6 (a) The laboratory co-ordinate system in which the target particle (of mass m_2) is initially at rest; v_c [as given by Eq. (125)] represents the velocity of the centre of mass. After scattering the two particles fly off in different directions. (b) In the centre of mass system, the two particles approach each other with the same momenta; the centre of mass is at rest.

(θ_0, φ_0); the target particle also suffers a recoil and moves in a different direction. In the centre of mass system, the centre of mass is at rest and the two particles will approach each other with velocities $m_2 v_1/(m_1 + m_2)$ and $-m_1 v_1/(m_1 + m_2)$. It is easy to see that the total momenta of the two particles before scattering is zero and hence they must fly off in opposite directions after scattering as shown in Fig. 19.6(b). In the centre of mass system, if the scattering angle is denoted by (θ, φ) then for elastic scattering (i.e., when kinetic energies are conserved) the particles should move away with their original speeds as shown in Fig. 19.6(*b*). In order to get back to the laboratory system we must superpose the velocity of the centre of mass which will readily give

$$v' \sin \theta_0 = \frac{m_2 v_1}{m_2 + m_1} \sin \theta$$

$$v' \cos \theta_0 = \frac{m_2 v_1}{m_1 + m_2} \cos \theta + v_c$$

$$\varphi = \varphi_0 \tag{126}$$

where v' is the speed of the particle of mass m_1 after scattering. Thus

$$\tan \theta_0 = \frac{\sin \theta}{m_1/m_2 + \cos \theta} \tag{127}$$

Notice that when $m_2 \gg m_1$, the centre of mass is almost at rest, $\theta_0 \simeq \theta$ and the two system of co-ordinates coincide.

Since the laboratory and centre of mass scattering angles are not equal, the angular distribution of the cross-section will be different in the two systems; the relation between the two scattering cross-sections can be obtained by noting that the number of particles scattered in a given element of solid angle must be the same in two systems; thus

$$\sigma(\theta_0, \varphi_0) \sin \theta_0 d\theta_0 d\varphi_0 = \sigma(\theta, \varphi) \sin \theta d\theta d\varphi \tag{128}$$

or using Eqs. (126) and (127)

$$\sigma(\theta_0, \varphi_0) = \frac{(1 + \gamma^2 + 2\gamma \cos \theta)^{3/2}}{|1 + \gamma \cos \theta|} \sigma(\theta, \varphi) \tag{129}$$

It is $\sigma(\theta, \varphi)$ which is obtained from the theory, the above equation tells us how to transform it to the laboratory system which should be compared with the experimental data.

PROBLEMS

Problem 19.1

Calculate the differential cross-section for the following potentials, using the Born approximation

(*a*) The square well potential

$$V(r) = -V_0 \quad \text{for } r < a$$
$$= 0 \quad \text{for } r > a$$

(*b*) The Gaussian potential

$$V(r) = -V_0 \exp\left[-\frac{1}{2}\left(\frac{r}{a}\right)^2\right] \tag{130}$$

You may have to use the relation

$$\int_0^\infty \exp(-\alpha t^2) \cos(2\beta t) dt = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \exp(-\beta^2/\alpha)$$

PROBLEM 19.2

The Yukawa potential is given by

$$V(r) = -g^2 \frac{e^{-\alpha r}}{r} \tag{131}$$

which is of the same form as the shielded Coulomb potential [see Eq. (51)] with g^2 playing the role of e^2 so that the dimensionless parameter $g^2/\hbar c$ measures the strength of the interaction. Assuming that the neutron-proton interaction can be described by a Yukawa potential (which is, however, not strictly true) and that $1/\alpha \sim 1.4 \times 10^{-13}$ cm, estimate $g^2/\hbar c$ from the observed zero energy cross-section of about 3.6×10^{-24} cm^2 (this is the triplet cross-section, see Sec. 19.7).

PROBLEM 19.3

Assume the charge distribution of a scatterer to be given by

$$Q(\mathbf{r}) = Z_1 e\, F(\mathbf{r}) \tag{132}$$

where $\int F(\mathbf{r})d\mathbf{r} = 1$ implying that the total charge of the scatterer is $Z_1 e$. Consider the scattering of a point charge $Z_2 e$, calculate $V_{\mathbf{q}}$ [see Eqs. (42) and (43)] by using the Poisson equation and show that

$$f(\theta) = -\frac{\mu}{2\pi\hbar^2} V_{\mathbf{q}} = \left(-\frac{\mu}{2\pi\hbar^2}\right) \frac{4\pi Z_2 e}{q^2}\, \Lambda(\mathbf{q}) \tag{133}$$

where

$$\Lambda(\mathbf{q}) = \int Q(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \tag{134}$$

PROBLEM 19.4

Using the results of the previous problem calculate $g(\mathbf{q})$ and hence the cross-section for a point charge for which

$$F(\mathbf{r}) = \delta(\mathbf{r})$$

Compare with the result obtained in Sec. 19.4.1.

PROBLEM 19.5

Use the results of Problem 19.3 to calculate $\sigma(\theta)$ for the following charge distributions

$$\begin{aligned}(a)\ Q(\mathbf{r}) &= \left(\frac{4\pi}{3} a^3\right)^{-1} (Z_1 e) \quad \text{for } r < a \\ &= 0 \qquad\qquad\qquad\quad \text{for } r > a \text{ (uniformly charged sphere)}\end{aligned} \tag{135}$$

$$(b)\ Q(\mathbf{r}) = \frac{Z_1 e}{(2\pi a^2)^{3/2}} e^{-r^2/2a^2} \qquad \text{Gaussian)} \tag{136}$$

$$(c)\ Q(\mathbf{r}) = \frac{Z_1 e}{4\pi a^2} \frac{1}{r} e^{-r/a} \qquad \text{(Shielded Coulomb)} \tag{137}$$

where $Z_1 e$ represents the total charge of the scatterer. Notice that all the cases will go over to the result of Problem 19.4 in the limit of $a \to 0$.

PROBLEM 19.6

The scattering of fast electrons by a complex atom can be, in many cases, represented fairly accurately by assuming the following form of the potential energy distribution

$$V = -\frac{Ze^2}{r} + Ze^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' \tag{138}$$

where the first term is the potential due to the nucleus and the second due to the atomic structure. For the hydrogen atom in the ground state, we may write

$$\rho(r) = |\psi(1s)|^2 = \frac{1}{\pi a_0^3} \exp(-2r/a_0)$$

Use the result of problem 19.3 to calculate $\sigma(\theta)$.

PROBLEM 19.7

Modify the analysis of the previous problem to study the scattering by helium atom, the ground state function of which can be represented by (see Sec. 12.4)

$$\psi_0 = \frac{Z^3}{\pi a_0^3} \exp[-Z(r_1 + r_2)/a_0], \quad Z = \frac{27}{16}.$$

PROBLEM 19.8

Referring to Fig. 19.6 show that the total energy in the laboratory and centre of mass systems are related by

$$E_c = \frac{m_2}{m_1 + m_2} E_l \tag{139}$$

PROBLEM 19.9

In the neutron-proton scattering, assuming that the range of the attractive force, a, to be approximately 3×10^{-13} cm show that the scattering will be almost isotropic (in the centre of mass system) for neutron energy $\lesssim$ 10 MeV. (This is indeed borne out by experimental data).

PROBLEM 19.10

Assuming the mass of neutron to be equal to the mass of the proton, prove that there cannot be any backscattering in the scattering of neutrons by protons.

PROBLEM 19.11

For neutron-proton scattering, make an angular distribution for $l = 0$ (s-wave), $l = 1$ (p-wave) and $l = 2$ (d-wave) scattering in the centre of mass and laboratory co-ordinate systems.

PROBLEM 19.12

For a short range force, use Eq. (92) to prove that

$$\frac{\delta_1}{\delta_0} \sim \frac{(ka)^2}{9}; \quad \frac{\delta_2}{\delta_0} \sim \frac{(ka)^4}{225}, \text{ etc.} \tag{140}$$

PROBLEM 19.13

Consider a repulsive potential given by

$$V(r) = V_0 \qquad 0 < r < a \qquad (141)$$
$$\quad = 0 \qquad r > a$$

show that

$$\delta_0 = \tan^{-1}\left[\frac{k}{K}\tanh Ka\right] - ka \qquad \text{for } E < V_0$$
$$= \tan^{-1}\left[\frac{k}{K_1}\tan K_1 a\right] - ka \qquad \text{for } E > V_0$$

where

$$k^2 = \frac{2mE}{\hbar^2}, \; K^2 = 2m(V_0 - E)/\hbar^2$$

and

$$K_1^2 = 2m(E - V_0)/\hbar^2$$

PROBLEM 19.14

For the square well potential discussed in Sec. 19.5.2 show that

$$\tan\delta_l = -\frac{kj_l'(ka) - \alpha_l j_l(ka)}{k\,n_l'(ka) - \alpha_l n_l(ka)} \qquad (142)$$

where

$$\alpha_l = \frac{Kj_l'(Ka)}{j_l(Ka)}$$

For $ka \ll 1$, using the forms of $j_l(\rho)$ and $n_l(\rho)$ for $\rho \to 0$, show

$$\delta_0 \approx \tan^{-1}\left[-\frac{\alpha_0 ka^2}{1 + \alpha_0 a}\right]$$

$$\delta_1 \approx \tan^{-1}\left[\frac{(ka)^3}{3}\,\frac{1 - \alpha_1 a}{2 + \alpha_1 a}\right], \text{ etc.}$$

PROBLEM 19.15

Obtain an expression for the coherent scattering cross-section for many scattering centres.

PROBLEM 19.16

Show that the total cross-section, Eq. (67), follows from Eq. (66) on using the orthogonality of Legendre polynomials.

PROBLEM 19.17

In elastic scattering there is no absorption of the incident particle by the scatterer. Thus the outgoing and incoming intensities must be equal. Equation (63) shows that this implies that δ_l must be real. Show that the reaction cross-section, defined as the number of particles removed from the beam per unit flux, is given by

$$\sigma_r = \sum_l \sigma_{r,l} = \sum_l \frac{\pi}{k^2} (2l + 1) (1 - |\eta_l|^2) \tag{143}$$

where $\eta_l = \exp(2i\delta_l)$ and η_l is called the collision amplitude. Show that while there can be scattering without absorption, there can be no absorption without scattering.

Problem 19.18

Prove the optical theorem

$$\sigma_{\text{total}} = \frac{4\pi}{k} \operatorname{Im} f(0) \tag{144}$$

where $\operatorname{Im} f(0)$ is the imaginary part of the forward scattering amplitude.

Problem 19.19

Consider the scattering of the wave packet

$$\Psi(\mathbf{r}, t_0) = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{k}\, a(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}} \tag{145}$$

by a fixed short-range potential. The wave packet described by the above equation is assumed to be localized well out of the range of the potential as shown in Fig. 19.7. Assuming that the particle is reasonably well localized in position space and at the same time has a fairly well defined momentum, calculate $\Psi(\mathbf{r}, t)$ at a time after the particle has been scattered by the target.

[*Hint*: Express $\Psi(\mathbf{r}, t_0)$ in terms or the exact eigenstates of the Schrödinger equation; Reference: Baym (1969)]

Problem 19.20

For the square well potential discussed in Sec. 19.2, show that the classical trajectory of the particle is the same as the path of a ray of light incident on a sphere of radius a with refractive index given by

$$n = \left(\frac{E + V_0}{E} \right)^{1/2} \tag{146}$$

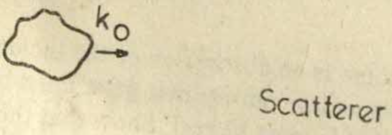

Fig. 19.7

PROBLEM 19.21

In the classical expression for the scattering cross-section for a square well potential [see Eq. (8)] if we let $V_0 \to \infty$ show that $\sigma(\theta)$ becomes independent of θ, i.e., the scattering becomes isotropic. For such a case show that the total cross-section is πa^2.

PROBLEM 19.22

For the Coulomb potential [see Eq. (95)] show that the relation between the impact parameter and the scattering angle is given by

$$s(\theta) = \frac{Z_1 Z_2 e^2}{2E} \cot \frac{\theta}{2} \tag{147}$$

(see, e.g., Goldstein, 1950 Sec. 3.7). Hence using Eq. (7)calculate the scattering cross-section.

SOLUTIONS

SOLUTION 19.1

$$(a) \quad \sigma(\theta) = \frac{4\mu^2 V_0^2}{\hbar^4 q^2} \left| \int_0^a \sin qr \; r \, dr \right|^2$$

$$= \frac{4\mu^2 V_0^2}{\hbar^4 q^6} (\sin qa - qa \cos qa)^2$$

where the symbols have the same meaning as in Sec. 19.4.

(*b*) Simple integration gives

$$\sigma(\theta) = \left(\frac{\mu}{2\pi \hbar^2} \right)^2 | V_q |^2 = \frac{2\pi\mu^2 a^6 V_0^2}{\hbar^4} e^{-q^2 a^2}$$

SOLUTION 19.2

Using Eq. (52), we get

$$\sigma = 2\pi \int_0^\pi \sigma(\theta) \sin \theta \, d\theta = 2\pi \int_0^{2k} \frac{4\mu^2 g^2}{\hbar^4 (q^2 + \alpha^2)^2} \frac{q dq}{k^2}$$

where we have used Eq. (45). On carrying out the integration, we get

$$\sigma = 16\pi \left(\frac{g^2}{\hbar c} \right)^2 \left(\frac{\mu c}{\hbar} \right)^2 \frac{1}{\alpha^4} \frac{1}{(1 + 4k^2/\alpha^2)}$$

or,

$$\sigma \xrightarrow[k \to 0]{} 16\pi \left(\frac{g^2}{\hbar c} \right)^2 \left(\frac{\mu c}{\hbar} \right)^2 \frac{1}{\alpha^4}$$

Using the data given in the problem and the fact that

$$\mu \approx \frac{m_n m_p}{m_n + m_p} \approx \frac{1}{2} m_p \approx 0.836 \times 10^{-28} \text{ g}$$

We get $g^2/\hbar c \sim 1.3$. This is very much larger than the 'strength' of electromagnetic coupling $e^2/\hbar c \sim 1/137$. However, the Yukawa potential is hardly a sufficiently accurate representation of the nuclear interaction and one should treat this value of $g^2/\hbar c$ as only a rough estimate.

SOLUTION 19.3

The Poisson equation is given by*

$$\nabla^2 V(\mathbf{r}) = -4\pi Z_2 e\, Q(\mathbf{r}) \tag{148}$$

Now, the Fourier transform of Eq. (43) gives

$$V(\mathbf{r}) = \frac{1}{8\pi^3} \int V_{\mathbf{q}}\, e^{i\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{q} \tag{149}$$

or,

$$\nabla^2 V = \frac{1}{8\pi^3} \int (-q^2)\, V_{\mathbf{q}}\, e^{i\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{q}$$

Thus

$$\frac{1}{8\pi^3} \int (-q^2 V_{\mathbf{q}})\, e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q} = -4\pi Z_2 e\, Q(\mathbf{r}) = -4\pi Z_2 e \frac{1}{8\pi^3} \int \Lambda(\mathbf{q})\, e^{i\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{q}$$

where in the last step we have used the Fourier transform of Eq. (134). Thus

$$V_{\mathbf{q}} = \frac{4\pi Z_2 e}{q^2} \Lambda(\mathbf{q}) \tag{150}$$

or

$$\sigma(\theta) = |f(\theta)|^2 = \left(\frac{\mu}{2\pi\hbar^2}\right)^2 \left|\frac{4\pi Z_2 e}{q^2} \Lambda(\mathbf{q})\right|^2 \tag{151}$$

SOLUTION 19.5

(*a*) $\Lambda(\mathbf{q}) = \int Q(\mathbf{r})\, e^{-i\mathbf{q}\cdot}\, d\mathbf{r}$

$$= \frac{Z_1 e}{\frac{4\pi}{3} a^3} \int_0^{2\pi} \int_0^{\pi} \int_0^{a} e^{-iqr\cos\theta}\, r^2 dr \sin\theta\, d\theta\, d\varphi$$

$$= \frac{3(Z_1 e)}{(qa)^3} [\sin qa - qa \cos qa] \tag{152}$$

---

*Two points ought to be mentioned here: first we are working here in the CGS units (because in the MKS units e should be replaced by q which would get confused with $\mathbf{q}$) and secondly in MKS units the Poisson equation is

$$\nabla^2 U = -\,[\text{charge density}]/\epsilon_0$$

where U is the potential (which is the potential energy per unit charge) and ϵ_0 is the free space permittivity [see, e.g., Reitz and Milford (1960)]. The final result obviously remains unchanged.

Hence

$$\sigma(\theta) = \left(\frac{2\mu}{\hbar^2}\right)^2 \frac{(Z_1 Z_2 e^2)^2}{q^4} \frac{9}{(qa)^6} [\sin qa - qa \cos qa]^2 \tag{153}$$

(*b*) $$\Lambda(\mathbf{q}) = Z_1 e \exp(-q^2a^2/2) \tag{154}$$

(*c*) $$\Lambda(\mathbf{q}) = \frac{Z_1 e}{(1 + q^2a^2)} \tag{155}$$

SOLUTION 19.6

Comparing with the notation of Problem 19.3, we have $Z_2 = -1$ and for the hydrogen atom $Q(\mathbf{r}) = e\delta(\mathbf{r}) - e\rho(\mathbf{r})$

$$\therefore \Lambda(\mathbf{q}) = [1 - F(q)] \tag{156}$$

where

$$\begin{aligned} F(q) &= \int \rho(\mathbf{r})\, e^{-i\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{r} \\ &= \frac{1}{\pi a_0^3} \iiint e^{-2r/a_0}\, e^{-iqr\cos\theta}\, r^2 dr \sin\theta\, d\theta\, d\varphi \\ &= \frac{1}{(1 + q^2a_0^2/4)^2} \end{aligned} \tag{157}$$

is sometimes called the atomic form factor. Substituting for $\Lambda(\mathbf{q})$ in Eq. (133) we get

$$\begin{aligned} \sigma(\theta) &= \left(\frac{2\mu e^2}{\hbar^2 q^2}\right)^2 [1 - F(q)]^2 = \frac{4}{a_0^2 q^4} [1 - F(q)]^2 \\ &= 4a_0^2 \frac{(8 + q^2a_0^2)^2}{(4 + q^2a_0^2)^4}, \quad q = 2k \sin\frac{\theta}{2} \end{aligned} \tag{158}$$

The total cross-section will be

$$\sigma = \int_0^{\pi} \sigma(\theta)\, 2\pi \sin\theta\, d\theta = \int_0^{2ka_0} \sigma(q) \frac{2\pi q\, dq}{k^2}$$

$$= \frac{8\pi}{k^2} \int_0^{2ka_0} \frac{(8 + y^2)^2}{(4 + y^2)^4}\, y dy$$

where $y = qa_0$. Writing

$$(8 + y^2)^2 = [4 + (4 + y^2)]^2 = 16 + 8\,(4 + y^2) + (4 + y^2)^2$$

We can easily carry out the integration. For $ka_0 \gg 1$, we obtain

$$\sigma \simeq \frac{7\pi}{3k^2} \tag{159}$$

SOLUTION 19.7

For the helium atom we have

$$V(r) = -\frac{2e^2}{r} + e^2 \int \sum_{n=1}^{2} \frac{1}{|\mathbf{r} - \mathbf{r}_n|} \, |\psi_0(\mathbf{r}_1, \mathbf{r}_2)|^2 \, d\tau_1 \, d\tau_2 \tag{160}$$

or

$$Q(\mathbf{r}) = 2e\,\delta(\mathbf{r}) - \frac{2Z^3}{\pi a_0^3} \exp\left[-2Zr/a_0\right] \tag{161}$$

Proceeding as in the previous problem we get

$$\sigma(\theta) = 16a_0^2 \frac{[8 \times (1.68)^2 + q^2a_0^2]^2}{[4 \times (1.68)^2 + q^2a_0^2]^4}. \tag{162}$$

Comparison of the theoretical results with experimental data show good agreement at electron energies above 100 eV (for further details, see Mott and Massey 1949).

SOLUTION 19.8

We refer to Fig. 19.6

$$E_{\text{lab}} = \tfrac{1}{2} m_1 v_1^2$$

and

$$E_{\text{cm}} = \frac{1}{2} m_1 \left(\frac{m_2 v_1}{m_1 + m_2}\right)^2 + \frac{1}{2} m_2 \left(\frac{m_1 v_1}{m_1 + m_2}\right)^2$$

$$= \frac{1}{2} \mu v_1^2 = \frac{m_2}{m_1 + m_2} E_{\text{lab}} \tag{163}$$

SOLUTION 19.9

Scattering will be predominantly s-wave ($l = 0$) for $ka \lesssim 1$ or

$$E_{\text{lab}} \approx 2E_{\text{cm}} \approx 2\left(\frac{\hbar^2 k^2}{2\mu}\right) \lesssim \frac{\hbar^2}{\mu a^2}$$

Thus

$$E_{\text{lab}} \lesssim \frac{(10^{-27})^2}{(0.8 \times 10^{-24}) \times (3 \times 10^{-13})^2} \approx 1.6 \times 10^{-5} \text{ erg} \approx 10 \text{ MeV} \tag{164}$$

SOLUTION 19.10

Equation (127) gives

$$\theta_0 = \theta/2$$

and since θ goes from 0 to π, θ_0 will be less than $\pi/2$.

SOLUTION 19.12

For a short-range force, only small values of r will contribute to the integral; therefore

$$\delta_l \approx -\frac{2\mu}{\hbar^2}\,\frac{(ka)^{2l+1}}{[1.3\ldots.(2l+1)]^2}\int_0^a V(r)\left(\frac{r}{a}\right)^{2l+1} r\,dr \tag{165}$$

where a denotes the range of the force, and we have made use of the formula

$$j_l \approx \frac{(kr)^l}{1.3\ldots.(2l+1)}$$

Evaluation of δ_l requires a knowledge of the potential, but an order of magnitude of the ratios is

$$\frac{\delta_1}{\delta_0} \sim \frac{(ka)^2}{9}; \quad \frac{\delta_2}{\delta_0} \sim \frac{(ka)^4}{225}, \text{ etc.}$$

SOLUTION 19.15

For a single scatterer, the asymptotic wave is given by

$$\psi \sim e^{ikz} - \frac{f}{r}\,e^{ikr}$$

If the scatterer is located at $\mathbf{r}_i$ then the distance to the detector is $|\mathbf{r} - \mathbf{r}_i|$ (see Fig. 19.8). There is, however, an extra phase change suffered by the incident wave by the time it reaches the scatterer so that

$$\psi^i_{sc} = -\frac{f_i}{|\mathbf{r} - \mathbf{r}_i|}\,e^{ikz_i}\,e^{ik|\mathbf{r}-\mathbf{r}_i|} \tag{166}$$

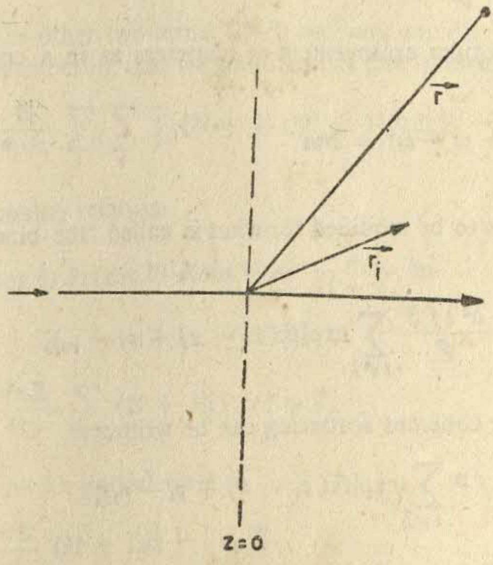

Fig. 19.8 If the scatterer is at $\mathbf{r}_i$, then the distance to the detector is $|\mathbf{r} - \mathbf{r}_i|$

The total intensity of the scattered wave is

$$
\begin{aligned}
|\psi_{sc}|^2 = \left|\sum \psi_{sc}^i\right|^2 &= \sum_{ij} f_i f_j^* \frac{\exp[ik(z_i - z_j)]}{\rho_i \rho_j} \exp[ik(\rho_i - \rho_j)] \\
&= \sum_i \frac{|f_i|^2}{\rho_i^2} + \sum_{i \neq j} f_i f_j^* \frac{\exp[ik(z_i - z_j + \rho_i - \rho_j)]}{\rho_i \rho_j} \qquad (167)
\end{aligned}
$$

where $\rho_i = |\mathbf{r} - \mathbf{r}_i|$. If we assume that all the scatterers are the same and their spread is much smaller than the distance of the detector, we can write

$$
|\psi_{sc}|^2 \approx \frac{N|f|^2}{\rho^2} + \frac{|f|^2}{\rho^2} \sum_{i \neq j} \exp[ik(z_i - z_j + \rho_i - \rho_j)] \qquad (168)
$$

where N is the number of scatterers. The first sum is the part that gives the incoherent scattering and the second the coherent scattering. Note that the second term in Eq. (168) is a double sum. The coherent part can give large variations with angle. If the scatterers are all randomly spaced, then the sum will average out to zero, if

$$
k \,\Delta \rho \gg 1
$$

where $\Delta\rho$ is roughly the spread of the scatterers. For $k\,\Delta\,\rho \sim 1$ one can get large values for coherent scattering. In the forward direction,

$$
\rho_i = z - z_i \quad \text{so that} \quad \rho_i - \rho_j = z_j - z_i
$$

Thus the coherent intensity is

$$
\left|\psi_{sc}\right|^2_{coh} \approx \frac{|f|^2}{\rho^2} N^2 \qquad (169)
$$

Again, if there is a regular arrangement of scatterers as in a crystal satisfying the condition

$$
k(z_i - z_j + \rho_i - \rho_j) = 2\pi n
$$

one gets maxima.

Equation (168) has to be modified for what is called 'the binding factor' in crystals. One writes

$$
\left|\psi_{sc}\right|^2_{coh} \approx \frac{b^2|f|^2}{\rho^2} \sum_{i \neq j} \exp[ik(z_i - z_j + \rho_i - \rho_j)] \qquad (170)
$$

The cross-section for coherent scattering can be written as

$$
\frac{d\sigma}{d\Omega} = b^2 |f|^2 \sum_{i \neq j} \exp[ik(z_i - z_j + \rho_i - \rho_j)]
$$

In those directions (Bragg angles) in which coherent scattering is appreciable,

$\sum_{i \neq j} \sim N^2$ (remembering that we have a double sum). Thus

$$\frac{d\sigma}{d\Omega} \sim N^2 b^2 |f|^2$$

SOLUTION 19.17

The net flux of particles through a sphere of radius R is given by [see Eq. (34) of Chapter 2]

$$j_R = \frac{\hbar}{2\mu i} \int \left[\psi^* \frac{\partial\psi}{\partial r} - \psi \frac{\partial\psi^*}{\partial r}\right]_{r=R} R^2 d\Omega \tag{171}$$

Now

$$\frac{\partial\psi}{\partial r} \underset{R\to\infty}{\rightarrow} \sum_l \frac{(2l+1)}{2ikR} P_l[e^{2i\delta_l} ik \cdot e^{ikR} + (-1)^l (ik) e^{-ikR}]$$

$$= \sum_l \frac{(2l+1)}{2R} P_l [\eta_l e^{ikR} + (-1)^l e^{-ikR}]$$

and

$$\psi^* \rightarrow \sum_l \frac{(2l+1)}{-2ikR} P_l[\eta_l^* e^{-ikR} - (-1)^l e^{ikR}]$$

We, now, cannot assume that η_l, η_l^* to be the same. Thus

$$\left[\psi^* \frac{\partial\psi}{\partial r}\right]_R = \sum_l \sum_{l'} \frac{(2l+1)P_l(2l'+1)P_{l'}}{-4ikR} [\eta_l \eta_{l'}^* - 1]$$
$$+ \text{ terms involving } e^{\pm 2ikR}$$

we can ignore the other two terms which oscillate rapidly and will average to zero. Thus (remembering that we want the net flux inward)

$$j_R = \frac{\hbar}{4\mu k} \sum_l \sum_{l'} \int (2l+1)(2l'+1) P_l P_{l'} [1 - \eta_l \eta_{l'}^*] \, d\Omega \tag{172}$$

Due to orthogonality relations

$$\int P_l(\cos\theta) P_{l'}(\cos\theta) \, d(\cos\theta) = \frac{2}{2l+1} \delta_{ll'}$$

we obtain

$$j_R = \frac{4\pi\hbar}{4k\mu} \sum_l (2l+1)[1 - |\eta_l|^2]$$

The current in the lth partial wave is

$$j_R = \frac{\pi\hbar}{\mu k} (2l+1)[1 - |\eta_l|^2] \tag{173}$$

Thus the reaction cross-section is

$$\sigma_r^l = \frac{\pi}{k^2}(2l+1)(1-|\eta_l|^2) \tag{174}$$

In Eq. (174), $|\eta_l| < 1$, for otherwise the outgoing current will exceed the incoming one. Since the scattering cross-section is

$$\sigma_{sc}^l = \frac{\pi}{k^2}(2l+1)\,|1-\eta_l|^2$$

one sees that σ_{sc}^l is largest for $\eta_l = -1$. In that case σ_r^l vanishes. On the other hand, $\eta_l = 0$ gives the maximum reaction cross-section for which

$$\sigma_{sc}^l = \sigma_r^l = \frac{(2l+1)\pi}{k^2}$$

If there is no scattering ($\eta_l = 1$), there clearly is no reaction either.

Solution 19.18

The total cross-section (from the previous problem) is

$$\sigma = \sigma_{el} + \sigma_r = \sum_l \sigma^l$$

where

$$\sigma^l = \frac{\pi}{k^2}(2l+1)[2-\eta_l-\eta_l^*]$$

$$= \frac{2\pi}{k^2}(2l+1)[1-\text{Re}\eta_l]$$

and $\text{Re}\eta_l$ is the real part of η_l. From Eq. (65) we have for the forward scattering amplitude,

$$f(0) = \sum_l (2l+1)\frac{\eta_l - 1}{2ik}$$

$$= i\sum_l (2l+1)\frac{(1-\eta_l)}{2k}$$

This establishes the optical theorem

$$\sigma = \frac{4\pi}{k}\,\text{Im}\,f(0)$$

CHAPTER 20

Time Dependent Perturbation Theory

20.1 Time Development of States

When a system is isolated and the Hamiltonian is independent of the time, the energy eigenstates are true stationary states. If the system initially is in a particular state Ψ_n which is an eigenstate of the Hamiltonian H_0, it will stay there for all time. The time dependence of Ψ_n is of the form

$$\Psi_n(t) = \Psi_n(0) \exp(-iE_n t/\hbar) \tag{1}$$

where E_n is the energy for the state n. If, however, the Hamiltonian is time dependent the energy is no longer a constant of motion. Knowledge of the behaviour of the system is obtained by solving the time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi = H\Psi \tag{2}$$

Unfortunately the structure of the Hamiltonian H in most cases does not permit a solution of this equation in closed form.

In many physical problems, the time dependence of the Hamiltonian arises because of what may be thought of as an external agency. An atom irradiated by light is an example. The time dependent part in such cases is usually a small perturbation representing the interaction of the system with the external agency. We may then write

$$H = H_0 + V(t) \tag{3}$$

where H_0 may be thought of as the sum of Hamiltonians of two systems in isolation and V, their interaction. Instead of attempting a direct solution of Eq. (2), we pose the problem in a slightly different manner. At a particular instant, say $t = 0$, the system may be regarded as being approximately in an eigenstate of H_0, labelled i. We would like to calculate the probability of finding the system in another state f, also an eigenstate of H_0 at a later time* t. Under these circumstances, we shall talk of the system being in quasi-stationary states. In most of the physical problems, we only have *quasi* stationary states. For example, an excited state of the hydrogen atom *does* decay and is not strictly a stationary state. At the other extreme, we may regard a state that lasts only for 10^{-20}s as quasi stationary; the point is that this lifetime may still be much longer than the natural frequencies of the system.

---

*If $V(t)$ acts for a finite duration, then the states i and f may be exact eigenstates of H_0 provided the perturbation is zero at the initial and final times of observation.

20.2 The Transition Probability

Let ψ_n denote the complete set of eigenkets of H_0

$$H_0\psi_n = E_n\psi_n = \hbar\omega_n\psi_n \tag{4}$$

where $E_n(= \hbar\omega_n)$ represent the corresponding energy eigenvalues. The wavefunction representing the actual state $\Psi(t)$ can be expanded in terms of ψ_n

$$\Psi(t) = \sum_n b_n(t)\psi_n(\mathbf{r})$$

where $| b_n(t) |^2$ can be interpreted as the probability of finding the system in the state n at time t. For the sake of convenience we write*

$$b_n(t) = C_n(t)\, e^{-i\omega_n t}$$

so that

$$\Psi(t) = \sum_n C_n(t)\, e^{-i\omega_n t}\, \psi_n(\mathbf{r}) \tag{5}$$

Obviously, $| C_n(t) |^2$ will also represent the probability of finding the system in the state n at time t. Our objective is to develop a perturbation theory for the calculation of $C_n(t)$ for a given $V(t)$. Now, from Eqs. (2), (3) and (5) we have

$$\begin{aligned} i\hbar \frac{\partial}{\partial t}\Psi(t) &= (H_0 + V)\,\Psi(t) \\ &= (H_0 + V)\sum_n C_n(t)\, e^{-i\omega_n t}\,\psi_n \\ &= \sum_n (E_n + V)\, C_n(t)\,\psi_n(\mathbf{r})\, e^{-i\omega_n t} \end{aligned} \tag{6}$$

where in the last step we have used Eq. (4). If we use Eq. (5), the left hand side of the above equation becomes

$$\begin{aligned} i\hbar \frac{\partial}{\partial t}\Psi(t) &= i\hbar \frac{\partial}{\partial t}\sum_n C_n(t)\, e^{-i\omega_n t}\,\psi_n \\ &= i\hbar \sum_n \left[\dot{C}_n - i\omega_n C_n \right] e^{-i\omega_n t}\,\psi_n \end{aligned}$$

Thus we have

$$i\hbar \sum_n \left[\dot{C}_n - i\omega_n C_n \right] e^{-i\omega_n t}\,\psi_n = \sum_n (E_n + V)\, C_n(t)\, e^{-i\omega_n t}\,\psi_n \tag{7}$$

---

*The rapidly varying term in $b_n(t)$ is the exponential term. Indeed if $V = 0$, $C_n(t)$ is independent of time.

where the second term on the left hand side cancels the first term on the right hand side. Multiplying on the left by ψ_s^* and remembering the orthonormality relation

$$\int \psi_s^* \psi_n \, d\tau = \langle s \mid n \rangle = \delta_{sn} \tag{8}$$

we get

$$i\hbar \frac{dC_s}{dt} = \sum C_n(t) \, V_{sn}(t) \exp(i\omega_{sn} t) \tag{9}$$

where

$$\omega_{sn} = \omega_s - \omega_n = \frac{E_s - E_n}{\hbar} \tag{10}$$

$$V_{sn}(t) = \int \psi_s^* \, V(t) \, \psi_n \, d\tau = \langle s \mid V \mid n \rangle \tag{11}$$

The set of equations (corresponding to various values of s) represented by Eq. (9) are exact. To solve them, we usually have to resort to perturbation techniques; there are, however, situations where one can obtain exact solutions of the time dependent equations; see, e.g., Problem 18.10, see also Problem 21.8.

Let us assume that at time t the amplitudes have not changed very much from their values at $t = 0$; i.e., we replace $C_n(t)$ by $C_n(0)$ on the right hand side of Eq. (9). We can then integrate Eq. (9) to give

$$i\hbar \, [C_s(t) - C_s(0)] = \sum_n C_n(0) \int_0^t V_{sn} \exp(i\omega_{sn} t) dt \tag{12}$$

We can apply this to the case where we know that the system is in a particular state i at $t = 0$. Thus

$$\begin{aligned} C_s(0) &= 1 \quad \text{for} \quad s = i \\ &= 0 \quad \text{for} \quad s \neq i \end{aligned} \tag{13}$$

so that

$$C_f(t) = \frac{1}{i\hbar} \int_0^t V_{fi}(t) \, e^{i\omega_{fi} t} \, dt, \quad f \neq i \tag{14}$$

Equation (14) gives the probability amplitudes at later times of states other than the initial one.

Suppose now that at $t = 0$ the perturbation is switched on and for $t > 0$, is independent of time*. Thus

$$C_f(t) = \frac{1}{i\hbar} V_{fi} \int_0^t \exp(i\omega_{fi} t) dt = - V_{fi} \frac{\exp(i\omega_{fi} t) - 1}{\hbar \omega_{fi}} \tag{15}$$

---

*In the next chapter, we will consider harmonic perturbations where $V(t)$ will vary sinusoidally with time and will describe the atom-field interaction.

Thus the probability for reaching the state f (at time t) is given by

$$P_f(t) = |C_f(t)|^2 = |V_{fi}|^2 \frac{1}{\hbar^2} \frac{\sin^2(\omega_{fi}t/2)}{(\omega_{fi}/2)^2} \tag{16}$$

We rewrite the above equation in terms of E_f and E_i:

$$P_f(t) = |V_{fi}|^2 \left[\frac{\sin(E_f - E_i)\,t/2\hbar}{(E_f - E_i)/2}\right]^2 \tag{17}$$

Figure 20.1 shows the behaviour of $P_f(t)$ as a function of E_f. We note the following :

(i) The perturabation theory result, viz. Eq. (17), is valid only when $P_f(t) \ll 1$.

(ii) As long as t is small enough such that

$$(E_f - E_i)\frac{t}{2\hbar} \ll 1 \tag{18}$$

the quantity $P_f(t)$ is proportional to t^2 for all values of E_f, in fact

$$P_f(t) \approx |V_{fi}|^2 \frac{t^2}{\hbar^2} \tag{19}$$

$$\text{(iii)} \quad \underset{E_f \to E_i}{\text{Lt}} P_f(t) = |V_{fi}|^2 \frac{t^2}{\hbar^2} \tag{20}$$

Equation (17) represents the probability of transition to one particular state ψ_f. In the applications that we would discuss, we would be interested in transitions to a group of closely spaced states. Thus the probability of transition to any one of the states is given by

$$W = \int P_f(t)\, \rho_f(E_f)\, dE_f \tag{21}$$

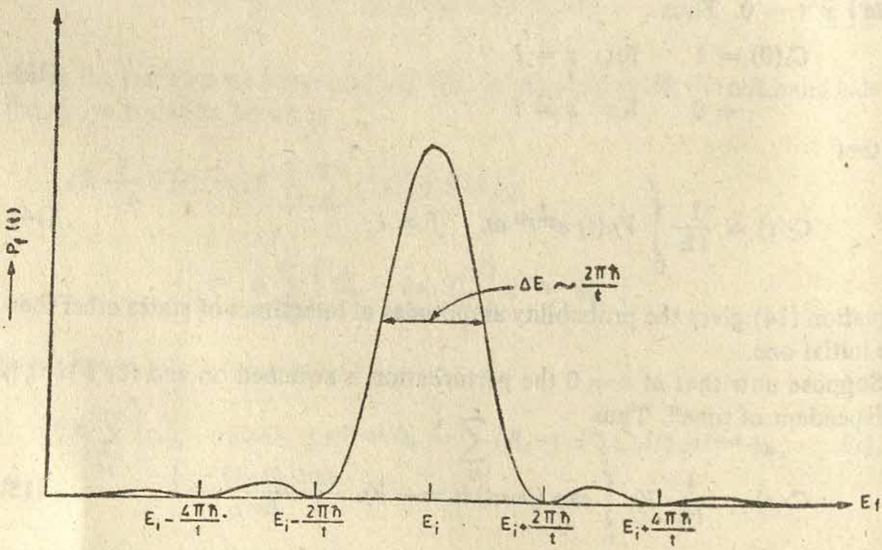

Fig. 20.1 The variation of $P_f(t)$ [$= |V_{fi}|^2 \sin^2(E_f - E_i)\,t/2\hbar \div \{(E_f - E_i)/2\}^2$ as a function of E_i. Notice that the function is peaked at $E_f = E_i$ with a width $\Delta E \sim \hbar/t$.

where $\rho(E_f)\, dE_f$ represents the number of final states in the energy interval dE_f. The density of states is usually a very smoothly varying function and since $P_f(t)$ is very sharply peaked around $E_f \approx E_i$, we may write

$$W \approx \rho_f(E_i) \int_{\Delta E} P_f(t)\, dE_f \tag{22}$$

where ΔE represents the central peak. We may now replace the limits of integration by $-\infty$ and $+\infty$ to obtain

$$W \approx \rho_f(E_i) \mid V \mid^2 \int_{-\infty}^{\infty} \left[\frac{\sin (E_f - E_i)\, t/2\hbar}{(E_f - E_i)/2} \right]^2 dE_f$$

$$\approx \rho_f(E_i) \frac{2t}{\hbar} \mid V \mid^2 \int_{-\infty}^{\infty} \frac{\sin^2 \xi}{\xi^2}\, d\xi$$

or $$W \approx \frac{2\pi}{\hbar} \mid V_{fi} \mid^2 \rho_f(E_i)\, t \tag{23}$$

The transition probability per unit time will be given by

$$\Gamma = \frac{dW}{dt} = \frac{2\pi}{\hbar} \mid V_{fi} \mid^2 \rho_f(E_i) \tag{24}$$

which is usually referred to as *Fermi's Golden Rule.* We illustrate the above procedure with a specific example. Suppose a system A undergoes a transition to two parts $A \rightarrow a + b$ due to a perturbation. Our question may be framed thus : If at time $t = 0$ we know that the system is in a specific state A, what is the probability that at a subsequent time $t > 0$, the system has 'decayed' into parts a and b? According to Eq. (17), there is a finite probability that the final state will have an energy $E_f \neq E_i$ (E_i was the energy at $t = 0$) where $E_f - E_i \lesssim \hbar/t$. Thus we must sum the probabilities over a set of states f within this interval—in fact, we shall sum over all states whatever the value of E_f. But, Eq. (17) ensures that the contribution from states for which $E_f - E_i \gg \hbar/t$ is negligible. We are, therefore, inevitably interested in the density of states f, i.e., the more states there are satisfying the relation $E_f - E_i \lesssim \hbar/t$ the more will be the transition probability.

If we assume that the entire system is in a box of volume V, we shall then have to calculate the number of states of a and b within an interval dE_f of a particular value E_f, say $\rho(E_f)\, dE_f$, compute the total probability for all these states and then integrate over all values of E_f. Equation (17) will ensure that we do not have to go far from $E_f = E_i$; i.e., we are essentially interested in the density of states $\rho(E_f = E_i)$.

We may mention here that in carrying out the integration in Eq. (23) we have assumed that t is large enough so that the function $P_f(t)$ is very sharply peaked around $E_f = E_i$ (so that ρ_f can be taken outside the integral); on the other hand, for the validity of perturbation theory, $P_f(t) \ll 1$, i.e., t should be small enough so that

$$\frac{|V_{fi}|^2}{\hbar^2}\, t^2 \ll 1 \tag{25}$$

We digress here to mention that since $P_f(t)$ is very sharply peaked around $E_f = E_i$, it should be possible to express it in the form of a delta function. Indeed, since

$$\operatorname*{Lt}_{g\to\infty} \frac{1}{\pi g}\, \frac{\sin^2 gx}{x^2} = \delta(x) \tag{26}$$

(see Appendix F), we may write

$$\operatorname*{Lt}_{t\to\infty} \frac{\sin^2 (E_f - E_i)\, t/2\hbar}{[(E_f - E_i)/2]^2} = \frac{\pi t}{\hbar}\, \delta\left(\frac{E_f - E_i}{2}\right)$$

$$= \frac{2\pi t}{\hbar}\, \delta(E_f - E_i) \tag{27}$$

Thus Eq. (17) gives

$$P_f(t) = \frac{2\pi}{\hbar}\, t\, |V_{fi}|^2\, \delta(E_f - E_i) \tag{28}$$

a formula which is often used. Equation (28) does appear nonsensical because it is zero for all values of $E_f \neq E_i$ and ∞ for $E_f = E_i$ and we know that $P_f(t)$ should be very small compared to unity. However, Eq. (28) has meaning only when it is multiplied by the smoothly varying function $\rho_f(E_f)$ and integrated over all energies to give Eq. (24).

20.3 Application to the Theory of Scattering

In Chapter 19 we discussed elastic scattering in which we considered the scattering of a wave packet by a fixed potential $V(\mathbf{r})$; this was done by obtaining a solution of the Schrödinger equation in the form of an incident plane wave and an outgoing scattered wave. Here we will consider another approach to the scattering problem by considering the scattering of a particle as a transition from an initial plane wave state to another plane wave state corresponding to a different direction of propagation. The two approaches will be shown to be equivalent although each approach has its own domain of application.

We consider a particle in a cube of volume L^3 and initially in a plane wave state corresponding to momentum $\mathbf{p}_i$. Thus the initial state of the particle is described by the wave function

$$\psi_i = \frac{1}{L^{3/2}} \exp[i\, \mathbf{k}_i \cdot \mathbf{r}] \tag{29}$$

where

$$\mathbf{k}_i = \frac{1}{\hbar}\, \mathbf{p}_i \tag{30}$$

It may be mentioned that by confining the particle inside a large box and by imposing the periodic boundary conditions (see Appendix M), the states become discrete; in fact the allowed values of k_x, k_y, and k_z are

$$k_x = \frac{2n_x\pi}{L},\ k_y = \frac{2n_y\pi}{L},\ k_z = \frac{2n_z\pi}{L} \tag{31}$$

where

$$n_x, n_y, n_z = 0, \pm 1, \pm 2, \pm 3, \ldots \tag{32}$$

We now assume that the perturbation $V(\mathbf{r})$ is switched on at $t = 0$. The probability of transition to the final state

$$\psi_f = \frac{1}{L^{3/2}} \exp(i\mathbf{k}_f \cdot \mathbf{r}) \tag{33}$$

is given by (see Eq. 17)

$$P_f(t) = |C_f(t)|^2 = |V_{fi}|^2 \left[\frac{\sin(E_f - E_i)t/2\hbar}{(E_f - E_i)/2} \right]^2 \tag{34}$$

where

$$\begin{aligned} V_{fi} &= \int \psi_f^* V \psi_i d\mathbf{r} \\ &= \frac{1}{L^3} \int V(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \end{aligned} \tag{35}$$

and

$$\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \tag{36}$$

Equation (34) represents the probability of the particle getting scattered to a particular state corresponding to $\mathbf{k}_f$. If we wish to get the total probability of the particle getting scattered into the solid angle $d\Omega$, which we will denote by $w d\Omega$, then we must multiply $P_f(t)$ by $\rho_f(E_f) dE_f d\Omega$ and integrate over all energies; here $\rho_f(E_f)\, dE_f\, d\Omega$ represents the number of states whose final energy lies between E_f and $E_f + dE_f$ and the direction of propagation in the solid angle $d\Omega$. Thus, using the method used in the previous section, we get

$$\begin{aligned} w d\Omega &= \int P_f(t)\, \rho_f(E_f)\, dE_f\, d\Omega \\ &\approx \frac{2\pi}{\hbar} |V_{fi}|^2 \rho_f(E_i)\, t d\Omega \end{aligned} \tag{37}$$

Thus the transition probability per unit time into the solid angle $d\Omega$ is given by

$$\Gamma d\Omega \approx \frac{2\pi}{\hbar} |V_{fi}|^2 \rho_f(E_i) d\Omega \tag{38}$$

Now, the density of final states is given by [see Eq. (10) of Appendix M]

$$\rho_f(E)\, dE\, d\Omega = \frac{L^3}{16\pi^3\hbar^3} (2m)^{3/2} E^{1/2}\, dE\, d\Omega \tag{39}$$

Further, since there is only one particle in volume L^3, the number of particles per unit volume will be $1/L^3$; thus the incident intensity, I, will be $1/L^3$ multiplied by their velocity $\hbar k/m$

$$I = \frac{1}{L^3}\,\frac{\hbar k}{m} = \frac{1}{L^3}\,\frac{(2mE)^{1/2}}{m} \tag{40}$$

From the definition of the cross-section (see Sec. 19.3) the number of particles scattered into the solid angle $d\Omega$ per unit time $= I\sigma d\Omega = \Gamma d\Omega$ or

$$\sigma d\Omega = \frac{\Gamma d\Omega}{I} = \frac{1}{(\hbar k/mL^3)}\left[\frac{2\pi}{\hbar}\,|\,V_{fi}\,|^2\,\rho_f(E_i)d\Omega\right] \tag{41}$$

or

$$\sigma d\Omega = \left(\frac{mL^3}{2\pi\hbar^2}\right)^2 |\,V_{fi}\,|^2\,d\Omega \tag{42}$$

Substituting for V_{fi} from Eq. (35), we get

$$\sigma = \left(\frac{m}{2\pi\hbar^2}\right)^2 \left|\int V(\mathbf{r})\,e^{-i\mathbf{q}\cdot\mathbf{r}}\,d\mathbf{r}\right|^2 \tag{43}$$

which is identical to the expression obtained by using the Born approximation [see Eq. (41) of Chapter 19]. This is to be expected because both employ first order perturbation theory.

20.4 Adiabatic Approximation

In this section we will consider the case of a perturbation varying slowly with time. For such a case if we can solve the eigenvalue equation

$$H(t)\,\psi_n(t) = E_n(t)\,\psi_n(t) \tag{44}$$

then we should expect that if at $t = 0$ the system is in the (non-degenerate) state $\psi_m(0)$ then at a later time the system will be in the state $\psi_m(t)$. We will show this explicity in this section and also calculate the probability of transitions to other states.

We assume the potential to be turned on from $t = -\infty$ so that the initial condition is [cf. Eq. (13)]

$$\begin{aligned} C_s(-\infty) &= 1 \quad \text{for } s = i \\ &= 0 \quad \text{for } s \neq i \end{aligned} \tag{45}$$

so that (cf. Eq. 14)

$$C_f(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} V_{fi}(t)\exp(i\omega_{fi}t)\,dt, \qquad f \neq i \tag{46}$$

Partial integration of Eq. 46 gives

$$C_f(t) = \left[- V_{fi} \frac{\exp(i\omega_{fi}t)}{\hbar\omega_{fi}} \right]_{-\infty}^{t} + \int_{-\infty}^{t} \frac{1}{\hbar\omega_{fi}} \frac{\partial V_{fi}}{\partial t} \exp(i\omega_{fi}t)\, dt$$

If we assume that $V_{fi}(t) \rightarrow 0$ as $t \rightarrow -\infty$, we can write

$$C_f(t) = - \frac{V_{fi}(t)}{\hbar\omega_{fi}} \exp(i\omega_{fi}t) + \int_{-\infty}^{t} \frac{1}{\hbar\omega_{fi}} \frac{\partial V_{fi}}{\partial t} \exp(i\omega_{fi}t)\, dt \tag{47}$$

The state of the system at the time t is given by (see Eq. 5)

$$\Psi(t) = C_i(t)\psi_i \exp(-i\omega_i t) + \sum_{f \neq i} C_f(t)\psi_f \exp(-i\omega_f t)$$

Assuming that the initial state has not been depleted very much in time t, we can put $C_i(t) \approx 1$. Substituting the values of $C_f(t)$ from Eq. (47), we obtain

$$\Psi(t) = \left[\psi_i - \sum_{f \neq i} \frac{V_{fi}}{\hbar\omega_{fi}} \psi_f \right] e^{-i\omega_i t}$$

$$+ \sum_{f \neq i} \int_{-\infty}^{t} \frac{1}{\hbar\omega_{fi}} \frac{\partial V_{fi}}{\partial t} \exp(-i\omega_{fi}t)\, \psi_f dt \tag{48}$$

The terms in the parenthesis in Eq. (48) represents the change in the state due to the application of a constant perturbation V (see Eqs. 13, 19 and 20 of Chapter 11) and has nothing to do with transitions. It is therefore the second term in Eq. (48) that gives transitions.

The *adiabatic approximation* is the assumption that the perturbation is turned on slowly, i.e., $\partial V_{fi}/\partial t$ is small. Equation (47) suggests the transitions to other states are extremely unlikely in this case. Assuming that $\partial V/\partial t \neq 0$ in an interval t_1 to t_2, we may write

$$C_f(t) \approx \frac{1}{\hbar\omega_{fi}} \left(\overline{\frac{\partial V_{fi}}{\partial t}} \right) \int_{t_1}^{t_2} e^{i\omega_{fi}t}\, dt$$

$$= \frac{1}{i\hbar\omega_{fi}^2} \left(\overline{\frac{\partial V_{fi}}{\partial t}} \right) [e^{i\omega_{fi}t_2} - e^{i\omega_{fi}t_1}] \tag{49}$$

The condition that $| C_f(t) | \ll 1$ gives

$$\frac{1}{\hbar\omega_{fi}^2} \frac{\partial V}{\partial t} \ll 1 \tag{50}$$

Since $\tau_{fi} = 1/\omega_{fi}$ is the period of the radiation in the transition, this statement implies that

$$\frac{1}{\hbar\omega_{fi}} \frac{\partial V}{\partial t} \ll \frac{1}{\tau_{fi}} \tag{51}$$

20.5 The Sudden Approximation

We next consider the case when the potential is turned on very rapidly, i.e.,

$$\tau \ll \tau_{fi} \sim \frac{1}{\omega_{fi}} \tag{52}$$

which implies that the time in which the perturbation changes appreciably is very small in comparison to the period involved in the transition. As an example, we assume

$$\begin{aligned} H &= H_0 \quad \text{for} \quad t < 0 \\ &= H_1 \quad \text{for} \quad t > 0 \end{aligned} \tag{53}$$

where H_0 and H_1 are independent of time. Let ψ_n and ϕ_n represent the orthonormal set of wavefunctions of H_0 and H_1 respectively. For $t < 0$, let the system be in an eigenstate of H_0 (say ψ_m). Since the Schrödinger equation is a first order equation in time, the wavefunction should be continuous at all times (although its time derivative need not be continuous). Now, at $t = 0$ we express ψ_m as a linear combination of ϕ_n

$$\psi_m = \sum_n a_n \phi_n \tag{54}$$

where

$$a_n = \int \phi_n^* \psi_m \, d\tau \tag{55}$$

represents the probability amplitude for transition to the state ϕ_n.

In general, in the sudden approximation we assume that $\partial V_{fi}/\partial t$ is essentially finite (and large) for a very small period of time say from T to $T + \tau$. During this time the exponent in the integral in Eq. (47) changes very little so that

$$C_f(t) \simeq \frac{1}{\hbar\omega_{fi}} e^{i\omega_{fi}T} \int_T^{T+\tau} \frac{\partial V_{fi}}{\partial t} \, dt = \frac{1}{\hbar\omega_{fi}} e^{i\omega_{fi}T} V_{fi} \tag{56}$$

Thus

$$| C_f(t) |^2 = \frac{1}{\hbar\omega_{fi}^2} | V_{fi} |^2 \tag{57}$$

From Eq. (56) we can see that the criterion for validity of sudden approximation is

$$\omega_{fi} \, \tau \ll 1 \tag{58}$$

The change of the perturbation in the sudden approximation looks somewhat as in Fig. 20.2.

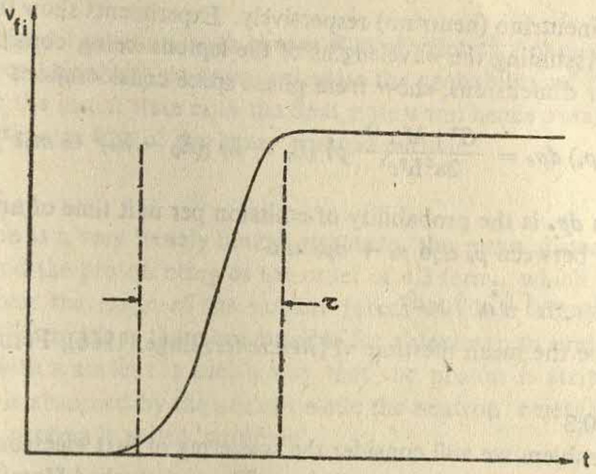

Fig. 20.2 A typical variation of the perturbation in the sudden approximation.

PROBLEMS

PROBLEM 20.1

The interaction of the neutron with a lattice can be well represented by the Fermi pseudo-potential

$$H' = \frac{2\pi\hbar^2}{m} \sum_n a_n \, \delta[\mathbf{r} - \mathbf{r}(n)] \tag{59}$$

where m is the mass of the neutron, a_n is known as the bound scattering length of the nth nucleus, $\delta(\mathbf{r})$ is the 3-dimensional Dirac δ-function, $\mathbf{r}(n)$ denotes the position of the nucleus and the summation is over all the nuclei in the lattice. Assume all the nuclei to have zero spin and no isotopes so that a_n is independent of n. Calculate the elastic scattering cross-section of neutrons by a simple cubic structure of lattice spacing d (neglect lattice vibrations). Show that the condition for non-vanishing scattering is that Bragg law be satisfied.
[*Hint*: For a simple cubic structure

$$\mathbf{r}(n) = d[n_1 \hat{\mathbf{x}} + n_2 \hat{\mathbf{y}} + n_3 \hat{\mathbf{z}}]$$

where n_1, n_2 and n_3 take integral values.]

PROBLEM 20.2

In the elementary theory of beta decay, the form of the interaction operator, H', is simply assumed to be a constant, which we denote by G. Thus the matrix element H'_{fi} of the interaction is defined as

$$H'_{fi} = G \int \psi^*_{fN} \, \psi^*_e \, \psi^*_\nu \, \psi_{iN} \, d\tau$$

where ψ_{iN} and ψ_{fN} are the normalized wavefunctions for the parent and daughter nucleus; ψ_e and ψ_ν are the normalized wavefunctions for the electron (positron) and the antineutrino (neutrino) respectively. Experiments show that $G \sim 10^{-48}$ g cm^5 s^{-2}. Assuming the wavelengths of the leptons being considerably longer than nuclear dimensions, show from phase space considerations that

$$P(p_e)\,dp_e = \frac{G^2\,|\,M_{fi}\,|^2}{2\pi^3\hbar^7c^3}\,p_e^2\,(E_0 - E)\,[(E_0 - E_e)^2 - m_\nu c^2]^{1/2}\,dp_e,$$

where $P(p_e)\,dp_e$ is the probability of emission per unit time of an electron with momentum between p_e and $p_e + dp_e$ and

$$M_{fi} = \int \psi^*_{fN}\,\psi_{iN}\,d\tau$$

What will be the mean life-time τ? [*Reference*: Enge (1966), Fermi (1950)].

Problem 20.3

In this problem we will consider the scattering of fast electrons by hydrogen atom; we will neglect exchange collisions. The unperturbed Hamiltonian is given by

$$H_0 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{r_2} \tag{60}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ represent the co-ordinates of the incident electron and the electron bound to the hydrogen atom respectively. The perturbation which causes the scattering will be given by

$$H' = \frac{e^2}{r_{12}} - \frac{e^2}{r_1} \tag{61}$$

where the two terms represent the incident electron–atomic electron interaction and the incident electron–atomic nucleus interaction respectively. Using the theory developed in Sec. 20.3 show that the scattering cross-section corresponding to the excitation of the hydrogen atom from the 1s state to the 2s state is given by

$$\sigma(\theta) = \frac{k_1}{k_0}\,\frac{128\,a_0^2}{[q^2a_0^2 + 9/4]^2} \tag{62}$$

where $a_0 = \hbar^2/me^2$,

$$q^2 = (\mathbf{k}_0 - \mathbf{k}_1)^2 = k_0^2 + k_1^2 - 2k_0\,k_1\cos\theta \tag{63}$$

θ is the scattering angle, $\hbar\mathbf{k}_0$ and $\hbar\mathbf{k}_1$ represent the momenta of the electron before and after the collision. (We may recall here that in Problem 19.6, we had discussed the elastic scattering of electrons by hydrogen atom; the present exercise is an example of inelastic scattering in which the energy of the scattered electron is different from the energy of the incident electron.)

Problem 20.4

A proton is travelling with an energy of 1 MeV in hydrogen gas. Estimate the minimum impact parameter for which there is appreciable energy transfer.

PROBLEM 20.5

Assuming that a heavy ion (with charge Z_1e) of velocity v passes undeflected as it suffers a collision with an atom, calculate the probability of transition of the atom from the initial state m to the final state n and hence obtain a formula for the rate of energy loss of the heavy charged particle.

PROBLEM 20.6

The deuteron is a very loosely bound structure, the mean distance between the neutron and the proton being of the order of 4.3 fermi, which is considerably larger than the range of the nuclear forces which is about 1.4 fermi. (1 fermi = 10^{-13} cm.) It is therefore possible for a deuteron to undergo a grazing collision with a nucleus in such a way that the proton is stripped off the deuteron and is absorbed by the nucleus while the neutron emerges as a free particle. This process is called 'stripping'.

(a) Show that for a deuteron energy of 200 MeV, this process is an example of a sudden transition.

(b) Calculate the energy distribution of the neutrons.

PROBLEM 20.7

Show that when the perturbation is small (sudden approximation) the probability amplitude given by Eq. (55) reduces to the expression given by Eq. (57).

PROBLEM 20.8

The radioactive H^3 nucleus decays to He^3,

$$H^3 \rightarrow He^3 + e^- + \nu$$

The electron energy is of the order of 10 keV. (It is actually a continuous spectrum but for most of it the above estimate is reasonable.) When a tritium atom decays, the He^3 is a structure with a single atomic electron which has to readjust its motion since the nuclear charge has changed. Show that the sudden approximation holds in this case and calculate the probability that the helium ion is in its ground state.

PROBLEM 20.9

Calculate the probability of excitation to the $2p$ state of a hydrogen atom, originally in its ground state, due to a homogeneous electric field with time-dependence

$$E = \frac{E_0}{\pi} \frac{\tau}{t^2 + \tau^2}$$

Discuss the limits of small and large values of τ and their significance.

PROBLEM 20.10

Let $|\psi(t)\rangle$ denote the state of a system at time t. Let $|n\rangle$ denote one of a complete set of eigenkets of an observable A, considered time-independent.

Derive the relation

$$i\hbar \frac{\partial C_n}{\partial t} = \sum_{n'} H_{nn'} C_{n'} \tag{64}$$

where $C_n(t)$ is the probability amplitude that the system is in the state $|n\rangle$ at the time t and $H_{nn'}$ is the matrix element $\langle n | H | n' \rangle$ of the Hamiltonian.

Problem 20.11

There are certain problems in which it is a reasonable approximation to assume that only a small number of states $|a\rangle$ are needed for the dynamical description of a system. This and the next two problems are examples of the two-state approximation*. The ammonia molecule has one nitrogen atom and three hydrogen atoms forming a pyramid (see Fig. 20.3). We now assume that the only two states of the molecule involved are (a) the state with the nitrogen atom above the plane of hydrogen atoms and (b) the state with nitrogen atom

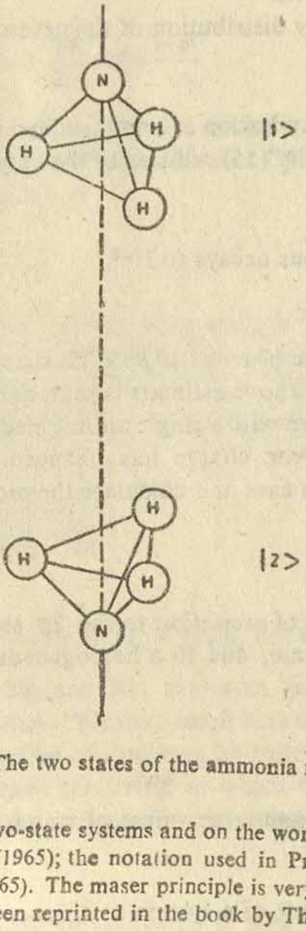

Fig. 20.3 The two states of the ammonia molecule.

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*For a nice discussion on two-state systems and on the working of the ammonia maser the reader is referred to Feynman (1965); the notation used in Problems 20.11 and 20.12 is the same as used by Feynman (1965). The maser principle is very nicely discussed in the Nobel lecture of Townes which has been reprinted in the book by Thyagarajan and Ghatak (1981). The K meson problem (see Problem 20.13) has been discussed at many places; see, e.g., Baym (1969), Feynmann (1965), Hughes (1972), etc.

below this plane. These are eigenstates of H_0, the major part of the Hamiltonian. But there is a small perturbation V, which couples the two states so that they are no longer eigenstates of the full Hamiltonian[*] $H = H_0 + V$. Assume

$$H_{11} = H_{22} = E_0,\ H_{12} = H_{21} = -A.$$

(a) Calculate the probabilities $|C_1(t)|^2$ and $|C_2(t)|^2$ that the molecule is in either of the two states at time t.
(b) What are the eigenstates of the Hamiltonian?
(c) Calculate the energy eigenvalues.

PROBLEM 20.12

The two states $|1\rangle$ and $|2\rangle$ of the ammonia molecule (see Fig. 20.3) have equal and opposite dipole moments. Thus in the presence of a static electric field we may write $H_{11} = E_0 + \mu\varepsilon$, $H_{22} = E_0 - \mu\varepsilon$, $H_{12} = H_{21} = -A$. Obtain the energies of the two stationary states.

PROBLEM 20.13

The K^0 is a meson produced in *strong interactions* such as

$$\pi^- + p \rightarrow \Lambda^0 + K^0$$

the K^0 state being an eigenstate of the strong interaction Hamiltonian. Similarly, the anti-particle $\bar{K}^0$ is also an eigenstate of the strong interaction Hamiltonian. On the other hand, in the absence of strong interactions (i.e., when the K^0 is all by itself and has no means of participating in strong interactions), the K^0 can decay via a weak interaction, the Hamiltonian for which may be regarded as very much smaller than the strong interaction Hamiltonian, $H_w \ll H_s$. As a result of H_w the K^0 and $\bar{K}^0$ are not eigenstates of the full Hamiltonian. As in Problem 20.11, we choose as the two base states (eigenstates of H_s) $|K^0\rangle$ and $|\bar{K}^0\rangle$. It turns out that the proper eigenstates are

$$|K_1^0\rangle = \frac{1}{\sqrt{2}}\left[\,|K^0\rangle + |\bar{K}^0\rangle\right] \tag{65}$$

and

$$|K_2^0\rangle = \frac{1}{\sqrt{2}}\left[\,|K^0\rangle - |\bar{K}^0\rangle\right] \tag{66}$$

This state $|K_1^0\rangle$ decays into $\pi^+ + \pi^-$ or $\pi^0 + \pi^0$ with a lifetime $\tau_1 \approx 0.9 \times 10^{-10}$ s. The lifetime of $|K_0^2\rangle$ which we denote by τ_2 is about 5.6×10^{-8} s. Thus we may write

$$\begin{aligned}|\Psi(t)\rangle = [C_1\,|K_1^0\rangle \exp(-iE_1t/\hbar)\exp(-t/2\tau_1)\\ + C_2\,|K_2^0\rangle \exp(-iE_2t/\hbar)\exp(-t/2\tau_2)]\end{aligned} \tag{67}$$

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[*] One may compare this problem with the double well problem discussed in Sec. 3.6.4. There we had seen that for a finite value of V_0, there is a coupling between the two wells and the levels split.

Since $\tau_2 \gg \tau_1$, assume $\tau_2 = \infty$ and calculate the probability that starting from a K^0 particle, we end up with a $\overline{K}_0$ particle at time t.

PROBLEM 20.14

(a) A quantum mechanical system (say a linear oscillator) is in a state $\psi_i(\mathbf{r})$ at $t = 0$ when it is subject to a large impulse $\mathbf{F}(t)$ of the form

$$\mathbf{F}(t) = \mathbf{P}\delta(t) \tag{68}$$

Show that immediately after the impulse, the wavefunction of the system is

$$\psi_f(\mathbf{r}) = \psi_i(\mathbf{r}) \exp [i\,\mathbf{P} \cdot \mathbf{r}/\hbar)$$

(b) Obtain an expression for the probability that, following the impulse, the system is found in the state n.

PROBLEM 20.15

Consider the reaction

$$A + a \rightarrow B + b$$

and the inverse reaction

$$B + b \rightarrow A + a$$

Show that, for the same centre of mass energies

$$\frac{\sigma_{A+a\rightarrow B+b}}{\sigma_{B+b\rightarrow A+a}} = \left(\frac{p_a}{p_b}\right)^2 \frac{(2S_B + 1)\,(2S_b + 1)}{(2S_A + 1)\,(2S_a + 1)} \tag{69}$$

where the momenta p_a and p_b are measured in the centre of mass system (c.m.s).

PROBLEM 20.16

Consider the nuclear reactions

$$p + p \rightarrow \pi^+ + d \tag{70}$$

and

$$\pi^+ + d \rightarrow p + p \tag{71}$$

where p, d and π^+ represent the proton, deuteron and π^+ meson respectively. If $\sigma_{pp\rightarrow\pi^+d}$ and $\sigma_{\pi^+d\rightarrow pp}$ represent the cross-sections for the processes described by Eqs. (70) and (71) at the same centre of mass energy, then using the results of the previous problem prove that

$$\sigma_{pp\rightarrow\pi^+d} = \frac{3}{2}\,\sigma_{\pi^+d\rightarrow pp}\,(2s_\pi + 1)\left(\frac{p_{\pi^+}}{p_p}\right)^2 \tag{72}$$

where S_π denotes the spin of the π-meson, p_p and p_{π^+} are the momenta of the proton and π^+ meson respectively.

PROBLEM 20.17

For an incident proton energy of 340 MeV, the cross-section of the reaction $pp \rightarrow \pi^+ d$ is found to be 0.18 ± 0.06 mb. In another experiment for an incident deuterium energy of 29 MeV, the cross-section of the reaction $\pi^+ d \rightarrow pp$ is found to be* 3.1 ± 0.3 mb. Show that

(i) both the reactions correspond approximately to the same centre of mass energy, and

(ii) that the pion spin is 0.

$$\begin{aligned}(m_{\pi^+} &= 139.6 \text{ MeV/c}^2 \\ m_p &= 938.3 \text{ MeV/c}^2 \\ m_d &= 1875.6 \text{ MeV/c}^2)\end{aligned}$$

PROBLEM 20.18

The K^+ meson has a decay mode

$$K^+ \rightarrow \pi^+ + \pi^+ + \pi^-$$

Assume that the decay rate can be calculated by the Golden Rule and that the matrix element causing the transition depends on the pion energies as

$$M \sim \frac{1}{\sqrt{\epsilon_1 \epsilon_2 \epsilon_3}}$$

where $\epsilon_1^2 = \sqrt{p_1^2 + m^2}$ is the total energy (including the rest energy) of the first π meson, etc. Calculate the energy distribution of the pions (say π^-) in the *rest system* of K.

SOLUTIONS

SOLUTION 20.1

The initial and final states of the neutron are given by

$$\frac{1}{L^{3/2}} \exp[i\mathbf{k}_0 \cdot \mathbf{r}]$$

and

$$\frac{1}{L^{3/2}} \exp[i\mathbf{k}_1 \cdot \mathbf{r}]$$

Since the scattering is elastic the initial and final states of the crystal are the

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*Data quoted from Hughes (1972). Experimental results are of Cartwright *et al.* (*Physical Review*, **91**, 667, 1953) and of Durbin *et al.* (*Physical Review*, 83, 646, 1951; **84**, 581, 1951).

same and $|\mathbf{k}_0| = |\mathbf{k}_1|$. The matrix element of transition is

$$H'_{fi} = \frac{2\pi\hbar^2 a}{mL^3} \int \exp[-i\mathbf{k}_1 \cdot \mathbf{r}] \sum_n \delta(\mathbf{r} - \mathbf{r}_n) \exp(i\mathbf{k}_0 \cdot \mathbf{r})\, d\mathbf{r}$$

$$= \frac{2\pi\hbar^2 a}{mL^3} \sum_n \int \exp[i\mathbf{k} \cdot \mathbf{r}]\, \delta(\mathbf{r} - \mathbf{r}_n)\, d\mathbf{r}$$

$$= \frac{2\pi\hbar^2 a}{mL^3} \sum_n \exp[i\mathbf{k} \cdot \mathbf{r}_n] \tag{73}$$

where

$$\mathbf{k} = \mathbf{k}_0 - \mathbf{k}_1 \tag{74}$$

The differential cross-section for scattering is therefore given by

$$\frac{d\sigma}{d\Omega} = \frac{1}{N} \left[\frac{1}{(\hbar k_0/m)\,(1/L^3)}\right] \left[\frac{2\pi}{\hbar}\, |H'_{fi}|^2\right] \left[\frac{m_0 k_1}{8\pi^3\hbar^2} L^3\right] \tag{75}$$

where the first bracketed term represents the incident flux and the last bracketed term the density of states. A factor $1/N$ is introduced to imply that $d\sigma/d\Omega$ is the differential cross-section per atom (N is the number of atoms in the crystal). For elastic scattering $|\mathbf{k}_0| = |\mathbf{k}_1|$ and one obtains

$$\frac{d\sigma}{d\Omega} = \frac{1}{N} a^2 \left| \sum_n \exp[i\mathbf{k} \cdot \mathbf{r}_n] \right|^2 \tag{76}$$

For a simple cubic lattice, the lattice points are given by

$$\mathbf{r}_n = d[n_1\hat{\mathbf{x}} + n_2\hat{\mathbf{y}} + n_3\hat{\mathbf{z}}]$$

where

$$n_\alpha = 0, 1, 2, \ldots N_\alpha - 1; \quad \alpha = 1, 2, 3 \ldots$$

i.e., the crystal consists of N_1, N_2 and N_3 atoms along the x, y and z axes, respectively and $N = N_1N_2N_3$ represents the total number of atoms. The origin is chosen at one of the corners of the crystal. Thus

$$\Delta = \left| \sum_n \exp[i\mathbf{k} \cdot \mathbf{r}_n)] \right|^2$$

$$= \left| \sum_{n_1=0}^{N_1-1} \sum_{n_2=0}^{N_2-1} \sum_{n_3=0}^{N_3-1} \exp[id(n_1k_x + n_2k_y + n_3k_z)] \right|^2$$

$$= \Delta_1\Delta_2\Delta_3 \tag{77}$$

where

$$\Delta_1 = \left| \sum_{n_1=0}^{N_1-1} e^{idn_1k_x} \right|^2 = \left| \frac{1 - e^{iN_1k_xd}}{1 - e^{ik_xd}} \right|^2$$

$$= \frac{\sin^2 (N_1k_xd/2)}{\sin^2 (k_xd/2)} \tag{78}$$

For large values of N_1 ($\approx 10^8$ in a typical crystal) the value of Δ_1 will be large ($=N_1^2$) if

$$\frac{k_xd}{2} = l\pi$$

l being an integer.

If $k_xd/2\pi$ differs from an integer by more than a few times $1/N_1$ then Δ_1 will be negligible. Thus, one obtains maximum scattering when

$$\begin{aligned} k_xd &= 2\pi l \\ k_yd &= 2\pi m \\ k_zd &= 2\pi n \end{aligned} \tag{79}$$

where l, m and n are integers (these are the Miller indices). Thus

$$k^2 = \frac{4\pi^2}{d^2} (l^2 + m^2 + n^2) \tag{80}$$

Further, using Eq. (74) we get

$$k^2 = k_0^2 - 2k_0k_1 \cos 2\theta + k_1^2 = 4k_0^2 \sin^2 \theta \tag{81}$$

where we have used the fact that $|\mathbf{k}_0| = |\mathbf{k}_1|$ and 2θ represents the scattering angle (see Fig. 20.4). Equating Eqs. (80) and (81) we get

$$2d \sin \theta = [l^2 + m^2 + n^2]^{1/2}\lambda \tag{82}$$

where $\lambda = 2\pi/k_0$. The above equation represents the Bragg condition for reflection from a set of planes of spacing $d/(l^2 + m^2 + n^2)^{1/2}$. A more detailed theory for elastic (as well as inelastic) scattering of neutrons from a simple Bravais lattice taking into consideration lattice vibrations has been given by Ghatak and Kothari (1972), Chapters 8 and 9.

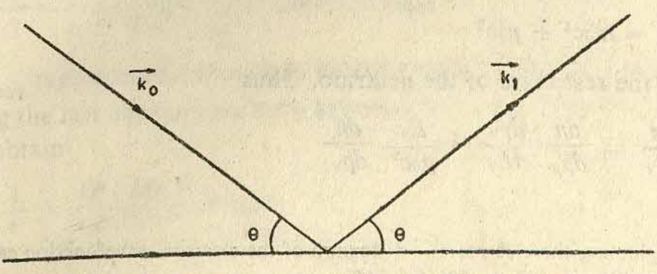

Fig. 20.4 Bragg scattering of neutrons by a crystal.

SOLUTION 20.2

Since the wavelength of the leptons are much larger than nuclear dimensions ($\approx 10^{-12}$ cm), we can replace the lepton wavefunctions with their value at the centre of the nucleus.* Now

$$\psi_e(r) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_e \cdot \mathbf{r}}$$

and

$$\psi_\nu(r) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_\nu \cdot \mathbf{r}}$$

so that at $r = 0$

$$\psi_e(0) = \psi_\nu(0) = \frac{1}{\sqrt{V}}$$

Thus

$$| H'_{fi} |^2 = \frac{G^2}{V^2} | M_{fi} |^2$$

where

$$M_{fi} = \int \psi^*_{fN} \psi_{iN} \, d\tau$$

Therefore, the probability of emission per unit time w, is,

$$w = \frac{2\pi}{\hbar} \frac{G^2}{V^2} \left| M_{fi} \right|^2 \frac{dn}{dE_0}$$

where

$$E_0 = E_e + E_\nu$$

E_e and E_ν representing the energies of electron and neutrino respectively. We first calculate the probability for the electron going into a particular state; then E_e is fixed and

$$\frac{dn}{dE_0} = \frac{dn}{dE_\nu}$$

Now

$$E_\nu^2 = m_\nu^2 c^4 + p_\nu^2 c^2$$

where m_ν is the rest mass of the neutrino. Thus

$$\frac{dn}{dE_\nu} = \frac{dn}{dp_\nu} \frac{dp_\nu}{dE_\nu} = \frac{E_\nu}{p_\nu c^2} \frac{dn}{dp_\nu}$$

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*We are neglecting the electrostatic distortion of the electron wavefunction caused by the charge on the nucleus; see Enge (1966) p. 315.

In Appendix M we have shown that the number of states for which the magnitude of the momentum has between p_ν and $p_\nu + dp_\nu$ is given by

$$\frac{V}{(2\pi\hbar)^3} 4\pi p_\nu^2 \, dp_\nu = \frac{V p_\nu^2 \, dp_\nu}{2\pi^2\hbar^3} \tag{83}$$

Thus

$$\frac{dn}{dE_0} = \frac{dn}{dE_\nu} = \left(\frac{E_\nu}{p_\nu c^2}\right) \frac{V p_\nu^2}{2\pi^2\hbar^3}$$

$$= \frac{V}{2\pi^2\hbar^3c^3} (E_0 - E_e) \left[(E_0 - E_e)^2 - (m_\nu c^2)^2\right]^{1/2}$$

and

$$W = \frac{G^2 \mid M_{fi} \mid^2}{\pi\hbar^4 c^3 V} (E_0 - E_e) \left[(E_0 - E_e)^2 - (m_\nu c^2)^2\right]^{1/2} \tag{84}$$

If $P(p_e)\, dp_e$ represents the probability (per unit time) of the momentum of the emitted electron to lie between p_e and $p_e + dp_e$, then in order to obtain $P(p_e)\, dp_e$ we must multiply the above expression for w by the number of electron states whose momenta lie between p_e and $p_e + dp_e$, this is given by (see Eq. 83) $Vp_e^2\, dp_e/2\pi^2\hbar^3$. Thus

$$P(p_e)\, dp_e = \frac{G^2 \mid M_{fi} \mid^2}{2\pi^3\hbar^7c^3} p_e^2 (E_0 - E_e) \left[(E_0 - E_e)^2 - (m_\nu c^2)^2\right]^{1/2} dp_e \tag{85}$$

The experimental data on the energy distribution of the emitted electrons show that the plot of $[P(p_e)/p_e^2]^{1/2}$ as a function of E_e is very nearly a straight line, which suggests that m_ν is zero or extremely small. A typical plot of $[P(p_e)/p_e^2]^{1/2}$ as a function of E_e corresponding to the $n \rightarrow p + \bar{e} + \bar{\nu}$ process is shown in Fig. 20.5; such a plot is known as the Kurie plot. The departure from the linearity is due to experimental errors and due to the finite velocity of the neutrons which undergo decay. We may mention here that for the β decay from nuclei of large Z values one should also consider the electrostatic distortion of the electron wavefunction (see Enge, 1966).

The expression for the mean life time is obtained by integrating Eq. (85) over all values of p:

$$\frac{1}{\tau} = \frac{G^2 \mid M_{fi} \mid^2}{2\pi^3\hbar^7c^3} \int_0^{p_{\text{max}}} p^2 \left[(m^2c^4 + p_{\text{max}}^2 c^2)^{1/2} - (m^2c^4 + p^2c^2)^{1/2}\right]^{1/2} dp$$

where p_{max} represents the maximum kinetic energy of the emitted electrons and in writing the last equation we have assumed $m_\nu = 0$. Carrying out the integration we obtain

$$\frac{1}{\tau} = \frac{G^2 \mid M_{fi} \mid^2}{2\pi^3\hbar^7c^3} F(\eta_0) \tag{86}$$

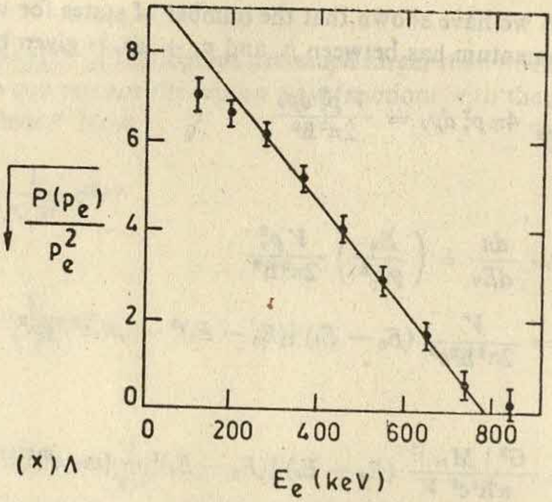

Fig. 20.5 The Kurie plot for the $n \to p + e^- + \bar{\nu}$ process. The disagreement between theory and experiment at low energies is due to experimental errors and also due to the fact that neutrons form a beam rather than a solid or liquid (adapted from Enge, 1966; the original data is of I. M. Robson, *Phys. Rev.* **83**, 349, 1951.)

where

$$F(\eta_0) = -\frac{1}{4}\eta_0 - \frac{1}{12}\eta_0^3 + \frac{1}{30}\eta_0^5 + \frac{1}{4}(1+\eta_0^2)^{1/2}\sinh^{-1}\eta_0 \quad (87)$$

and $\eta_0 = p_{\max}/mc$. Equation (86) tells us that if $|M_{fi}|^2$ does not change, the value of $F\tau$ must be a constant for different β-emitters; this is approximately borne out from experimental data (see, e.g., Born, 1962; Enge, 1966).

SOLUTION 20.3*

The initial and final states of the system, which are eigenfunctions of H_0, are given by

$$\psi_i = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\,\psi_{100}(\mathbf{r}_2)$$

and

$$\psi_f = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_1\cdot\mathbf{r}_1}\,\psi_{200}(\mathbf{r}_2)$$

Energy conservation demands that

$$\frac{\hbar^2 k_0^2}{2m} - \frac{me^4}{2\hbar^2} = \frac{\hbar^2 k_1^2}{2m} - \frac{me^4}{8\hbar^2}$$

---

*The solution adapted from Schiff (1955) Sec. 30; used with permission from McGraw-Hill Book Company.

or

$$k_1^2 = k_0^2 - \frac{3m^2e^4}{8\hbar^4}$$

Now, the matrix element for the transition is given by

$$H'_{fi} = \frac{1}{V}\iint e^{-i\mathbf{k}_1\cdot\mathbf{r}_1}\,\psi^*_{200}(\mathbf{r}_2)\left[\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}-\frac{e^2}{\mathbf{r}_1}\right]e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\,\psi_{100}(\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2$$

Since

$$\int \psi^*_{200}(\mathbf{r}_2)\,\psi_{100}(\mathbf{r}_2)\,d\mathbf{r}_2 = 0$$

the integral involving $e^2/\mathbf{r}_1$ would vanish. Thus

$$H'_{fi} = \frac{e^2}{V}\int \psi^*_{200}(\mathbf{r}_2)\,\psi_{100}(\mathbf{r}_2)\,I(\mathbf{r}_2)\,d\mathbf{r}_2 \tag{88}$$

where

$$I(\mathbf{r}_2) = \int \frac{e^{i\mathbf{q}\cdot\mathbf{r}_1}}{|\mathbf{r}_1-\mathbf{r}_2|}\,d\mathbf{r}_1 = e^{i\mathbf{q}\cdot\mathbf{r}_2}\iiint \frac{e^{iq\rho\cos\theta}}{\rho}\,\rho^2\,d\rho\,\sin\theta\,d\theta\,d\varphi$$

where $\rho = \mathbf{r}_1 - \mathbf{r}_2$ and in carrying out the integration we have assumed the z axis to be along $\mathbf{q}$. Carrying out the integrations over θ and φ we get

$$I(\mathbf{r}_2) = \frac{4\pi}{q}\,e^{i\mathbf{q}\cdot\mathbf{r}_2}\int_0^\infty \sin q\rho\,d\rho$$

The above integral does not have a well-defined value. In order to evaluate the integral we introduce an exponentially decaying factor $e^{-\lambda\rho}$ to carry out the integration and take the limit $\lambda \to 0$ to obtain*

$$I(\mathbf{r}_2) = \frac{4\pi}{q}\,e^{i\mathbf{q}\cdot\mathbf{r}_2}\,\underset{\lambda\to 0}{\mathrm{Lt}}\int_0^\infty \sin q\rho\,e^{-\lambda\rho}\,d\rho = \frac{4\pi}{q^2}\,e^{i\mathbf{q}\cdot\mathbf{r}_2} \tag{89}$$

*Such a procedure is justified because when $r_1 \gg r_2$

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \to \frac{1}{r_1}\left[1 + \hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\,\frac{r_2}{r_1}\right] = \frac{1}{r_1} + \hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2\,\frac{r_2}{r_1^2}$$

and therefore, if we first carry out the integration over $\mathbf{r}_2$ then the result will fall off as $1/r_1^2$; the integral containing the term $1/r_1$ will vanish because of orthogonality of ψ_{100} and ψ_{200}. Thus for large r_1 the integrand will fall of as $\sin qr_1/r_1$ making the integral convergent.

Substituting the above result and the hydrogen atom wavefunctions in Eq. (88) we get

$$H'_{fi} = \frac{e^2}{V}\int d\mathbf{r}_2 \left[\left\{\left(\frac{1}{32\pi a_0^3}\right)^{1/2}\left(2 - \frac{r_2}{a_0}\right)e^{-r_2/2a_0}\right\}\left\{\left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r_2/a_0}\right\}\frac{4\pi}{q^2}\, e^{i\mathbf{q}\cdot\mathbf{r}_2}\right]$$

where $a_0 = \hbar^2/me^2$. Once again we choose the z_2 axis along $\mathbf{q}$ and carry out the straightforward integrations to obtain

$$H'_{fi} = \frac{1}{V}\,\frac{16\sqrt{2}\,\pi a_0^2 e^2}{(q^2 a_0^2 + 9/4)^3}$$

The differential cross-section can now be obtained by using the formulae given in Sec. 20.3; however, we must remember that in calculating I (see Eq. 40) we should use k_0 and in calculating ρ_f (see Eq. 39) we should use k_1; consequently

$$\sigma(\theta) = \frac{k}{k_0}\left(\frac{m}{2\pi\hbar^2}\right)^2 V^2\,|H'_{fi}|^2 \tag{90}$$

from which one immediately gets Eq. (62). A nice discussion on the total cross-section has been given by Schiff (1955), Sec. 30. One can similarly calculate the scattering cross-section for the 1 $S \rightarrow 2P$ transition.

SOLUTION 20.4

Assume that the impact parameter is d (Fig. 20.6); the collision time, the time for which the potential energy changes appreciably, is of the order of $2d/v$ where v is the velocity of the proton. The change in potential energy is of the order e^2/d. If $\hbar\omega$ is the energy required for excitation to the $n = 2$ state of the atom, Eq. (51) suggests that a transition will occur only if

$$\frac{\partial V}{\partial t} \gtrsim \hbar\omega^2$$

or

$$\frac{ve^2}{2d^2} \gtrsim \hbar\omega^2$$

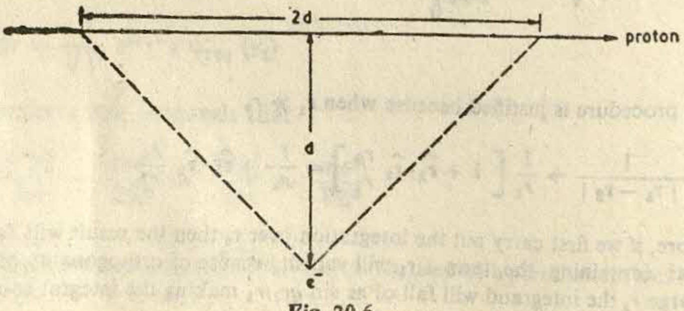

Fig. 20.6

Thus

$$2d^2 \leqslant \frac{ve^2\hbar}{(\hbar\omega)^2}$$

Putting $\hbar\omega \sim 10$ eV, we get the estimate

$$d \leqslant 2.5\ \text{Å}$$

SOLUTION 20.5

We assume that the heavy ion of charge Z_1e, velocity v passes undeflected even as it suffers a collision with an atom (Fig. 20.7). If each atom of the medium (assumed to be of a single element) has Z_2 electrons, the potential energy is

$$V = Z_1e^2 \sum_{i=1}^{Z_2} \frac{1}{|\mathbf{r}_i - \mathbf{R}|} \tag{91}$$

Assuming $|\mathbf{r}_i| \ll |\mathbf{R}|$, we can write

$$V \approx \frac{Z_1e^2}{R} \sum_i \left(1 + \frac{r_i}{R}\, \hat{\mathbf{r}}_i \cdot \hat{\mathbf{R}}\right) \tag{92}$$

In this expression, we treat r_i as stationary and $R(t)$ alone as a function of time. This is in the spirit of the sudden approximation; it can be shown that if the collision is adiabatic there is no loss of energy. We assume that at $t = 0$, the ion passes closest to the centre of the atom, the impact parameter being ρ. We take the co-ordinates of $\mathbf{R}$ to be $(vt, \rho, 0)$, of $\mathbf{r}_i$ to be (x_i, y_i, z_i) so that

$$V = \frac{Z_1e^2}{R} \sum_i \left[1 + \frac{1}{R^2}(x_i\, vt + \rho y_i)\right] \tag{93}$$

We have to calculate matrix elements $\langle n | V | m \rangle$ where m, n are the initial and

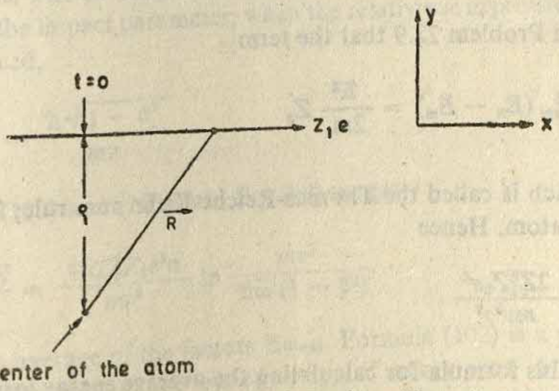

Fig. 20.7 Collision of a heavy ion with an atom

final states of the atom. It is clear that the first term in (93) contributes nothing. We obtain

$$V_{nm} = \frac{Z_1 e^2}{R^3} \left[(\Sigma x_i)_{nm}\, vt + (\Sigma y_i)_{nm}\, \rho \right] \tag{94}$$

The transition probability is $|C_{nm}|^2$ where

$$C_{nm} = -\frac{i}{\hbar} \int_{-\infty}^{\infty} V_{nm} \exp(i\omega_{nm}t)\, dt \tag{95}$$

For $\omega_{nm}t \ll 1$, we can replace the exponential by unity. The first term in (94) being odd in t, vanishes and

$$C_{nm} = -\frac{iZ_1e^2}{\hbar} \int_{-\infty}^{\infty} \frac{\rho(\Sigma y_i)_{nm}}{(\rho^2 + v^2t^2)^{3/2}}\, dt \tag{96}$$

The integral is easily evaluated by setting $vt = \rho \tan\theta$. We get

$$C_{nm} = -\frac{i}{\hbar} Z_1 e^2 \frac{1}{v\rho}\, 2y_{nm}$$

where $y_{nm} = (\Sigma y_i)_{nm}$ is the y component of the dipole matrix element. The transition rate is

$$|C_{nm}|^2 = \frac{4Z_1^2 e^4}{\hbar^2} \frac{1}{v^2\rho^2}\, y_{nm}^2$$

The average energy loss by the ion in such excitations of the atom is (assuming that m is always the ground state)

$$\overline{\mathcal{E}} = \sum_n (E_n - E_m)\, |C_{nm}|^2 = \frac{4Z_1^2 e^4}{\hbar^2} \frac{1}{v^2\rho^2} \sum_n y_{nm}^2 (E_n - E_m) \tag{97}$$

It is shown in Problem 22.9 that the term

$$\sum_n y_{nm}^2 (E_n - E_m) = \frac{\hbar^2}{2m} Z_2$$

a relation which is called the Thomas-Reiche-Kuhn sum rule; Z_2 is the charge of the target atom. Hence

$$\overline{\mathcal{E}} = \frac{2Z_1^2 Z_2 e^4}{mv^2\rho^2} \tag{98}$$

We now use this formula for calculating the average energy loss $-dE$ as the ion traverses a length dx of the medium. The number of collisions with atoms such that the impact parameter lies between ρ and $\rho + d\rho$ is

$$2\pi n \, \rho d\rho \, dx$$

where n is the number of atoms per unit volume. The energy loss in dx is

$$-dE = \int_{\rho_{\min}}^{\rho_{\max}} \frac{2Z_1^2 Z_2 e^4}{mv^2 \rho^2} 2\pi n\rho \, d\rho \, dx$$

or

$$-\frac{dE}{dx} = \frac{4\pi Z_1^2 Z_2 e^4 n}{mv^2} \ln\left(\frac{\rho_{\max}}{\rho_{\min}}\right) \tag{99}$$

In order to decide on the limits $\rho_{\max}$ and $\rho_{\min}$ we use the following arguments. Referring to Eqs. (95) and (96), we can write

$$C_{nm} \sim \int \frac{\exp(i\omega_{nm} t)}{(t^2 + \rho^2/v^2)^{3/2}} dt$$

so that if $\rho/v \gg 1/\omega_{nm}$, we can, in fact, take out the denominator from the integral and $C_{nm} \to 0$ since we shall be averaging over several periods even for small t. This, in fact, is the adiabatic limit. We therefore set ρ at this limit.

$$\rho_{\max} = \frac{v}{\omega_{nm}}$$

It can be shown that when relativistic effects are included we should correct this to

$$\rho_{\max} = \frac{v}{\omega_{nm}\sqrt{1-\beta^2}}; \ \beta = \frac{v}{c} \tag{100}$$

For $\rho_{\min}$ we note that the heavy ion 'sees' electrons moving towards it with momenta $\sim mv$. The de Broglie wavelength is $\sim \hbar/mv$. This must be the minimum value of the impact parameter; when the relativistic expression for momentum is introduced,

$$\rho_{\min} = \frac{\hbar\sqrt{1-\beta^2}}{mv} \tag{101}$$

Inserting Eqs. (100) and (101) into Eq. (99) we get

$$-\frac{dE}{dt} = \frac{4\pi Z_1^2 Z_2 e^4 n}{mv^2} \ln \frac{mv^2}{\hbar\bar{\omega}\,(1-\beta^2)} \tag{102}$$

where $\hbar\bar{\omega}$ is an average of the factors $\hbar\omega_{nm}$. Formula (102) is a simplified version of Bohr's treatment of the loss of energy of heavy ions in matter; it has important applications in nuclear physics where it is often necessary to know how much energy is deposited by particles as they go through matter.*

SOLUTION 20.6

[*Reference*: R. Serber, *Phys. Rev.* 72, 1008 (1947)]. We neglect the effect of Coulomb interactions and assume that the collision time $\tau = r_0/v$ where r_0 is the range of the nuclear forces and v the deuteron velocity. The transition here is from the bound deuteron to the continuum, the relevant period being about $\omega \sim \mathcal{E}_d/\hbar$ where $\mathcal{E}_d$ is the binding energy of the deuteron. Now $E_d = \frac{1}{2}(2M)v^2$ so that

$$\omega\tau = \frac{r_0}{v}\frac{\mathcal{E}d}{\hbar} = r_0\sqrt{\frac{M}{E_d}}\frac{\mathcal{E}_d}{\hbar}$$

The deuteron binding energy can be expressed in terms of its 'radius' $r_d = \hbar/\sqrt{M\mathcal{E}_d}$ so that

$$\omega\tau = \frac{r_0}{r_d}\sqrt{\frac{\mathcal{E}_d}{E_d}} \ll 1 \text{ (for } E_d \sim 200 \text{ MeV and } \mathcal{E}_d \sim 2.2 \text{ MeV)}$$

which suggests that the collision may be regarded as sudden.

In the centre of mass system of the deuteron, the state of the neutron changes from

$$\psi_i = \frac{\alpha}{\sqrt{2\pi}}\frac{e^{-\alpha r}}{r} \quad \text{to} \quad \psi_f \sim A\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar) \tag{103}$$

where $\alpha = \sqrt{M\mathcal{E}_d}/\hbar$, M is the mass of the neutron. ψ_i is the wavefunction of the deuteron outside the range of the nuclear force. But, as mentioned in the problem, since the deuteron size is much larger than the range, we can treat ψ_i as valid for the entire space. ψ_f is the wavefunction for the free neutron, A a constant of normalization.

The probability for the transition is

$$P(p)\,d\mathbf{p} = \frac{A^2\alpha^2}{2\pi}\left|\int \exp(-i\mathbf{p}\cdot\mathbf{r}/\hbar)\frac{e^{-\alpha r}}{r}\,d\mathbf{r}\right|^2 d\mathbf{p}$$

$$= \frac{A^2\alpha^2}{2\pi}\left|\int_0^\infty\int_0^{2\pi}\exp(-ipr\cos\theta/\hbar)\exp(-\alpha r)r\,dr\,2\pi\sin\theta\,d\theta\right|^2 d\mathbf{p}$$

$$= \frac{A^2\alpha^2}{2\pi}\left|4\pi\hbar\int_0^\infty dr\,\frac{e^{-\alpha r}}{p}\sin\frac{pr}{\hbar}\right|^2 d\mathbf{p} \tag{104}$$

---

*A more complete treatment was given by H.A. Bethe in *Annals Phys.* 5, 325 (1930).

Now

$$\int_0^\infty \sin kr\, e^{-\alpha r}\, dr = \operatorname{Im}\left[\int_0^\infty e^{ikr}\, e^{-\alpha r}\, dr\right] = \operatorname{Im}\frac{1}{ik-\alpha} = \frac{k}{k^2+\alpha^2}$$

Thus

$$P(\mathbf{p})\, d\mathbf{p} = B\,\frac{d\mathbf{p}}{\{(p^2/\hbar^2)+\alpha^2\}^2} \tag{105}$$

We now wish to transform the expression to the lab system in which the centre of mass of the deuteron moves along the z-direction with a velocity v where

$$\tfrac{1}{2}\,(2M)\,v^2 = E_d$$

If we write

$$p^2 = p_z^2 + p_\perp^2 \tag{106}$$

then, to the z-component we have to add the momentum of the centre of mass,

$$p_0 = Mv = \sqrt{ME_d}$$

(we neglect relativistic effects). The distribution in p_z is (from Eq. 105)

$$P(p_z)\, dp_z = B dp_z \int_0^\infty \frac{p_\perp\, dp_\perp}{[\{(p_\perp^2+p_z^2)/\hbar^2\}+\alpha^2]^2} = \frac{B' dp_z}{(\hbar^2\alpha^2+p_z^2)} \tag{107}$$

We can relate p_z to the neutron and deuteron energies in the lab system. If $\mathbf{p}_n$ is the neutron momentum in the lab system, we have

$$\mathbf{p}_n = \mathbf{p} + \mathbf{p}_0 \qquad \text{where} \qquad p \ll p_0 \tag{108}$$

(The momenta p are the Fourier components of the deuteron wavefunction. Since the deuteron is a very loosely bound structure, these momenta are very much smaller than the kinetic energy of the deuteron.) From Eq. (108) we get

$$p_n^2 = p^2 + p_0^2 + 2p_0p_z \approx p_0^2 + 2p_0p_z$$

In terms of the neutron energy $E = p_n^2/2M$ deuteron energy $E_d = p_0^2/M$ this gives

$$E = \frac{E_d}{2} + \sqrt{\frac{E_d}{M}}\, p_z \tag{109}$$

Thus Eq. (107) gives

$$P(E)\, dE \propto \frac{dE}{\hbar^2\alpha^2 + (M/E_d)\,(E - E_d/2)^2}$$

Writing $\hbar^2\alpha^2 = M\mathcal{E}_d$, we obtain

$$P(E)\,dE = C\frac{dE}{(E - \frac{1}{2}E_d)^2 + \mathcal{E}_d E_d} \tag{110}$$

This is a distribution which is peaked around $E = \frac{1}{2}E_d$ with a width of $\Delta E = 2\sqrt{\mathcal{E}_d E_d}$. Moreover, it goes to a very small value for $E = 0$ so that we can normalize it by integrating Eq. (110) from $E = -\infty$ to $+\infty$. This gives

$$1 = C\frac{\pi}{\sqrt{\mathcal{E}_d E_d}}$$

so that the normalized distribution is

$$P(E)\,dE = \frac{\sqrt{\mathcal{E}_d E_d}}{\pi}\,\frac{dE}{(E - \frac{1}{2}E_d)^2 + \mathcal{E}_d E_d}$$

The experimental distribution for $E_d = 200$ MeV agrees very closely with this expression with the peak at 95 MeV and a width of about 45 MeV. The above theory predicts a width of $2\sqrt{\mathcal{E}_d E_d} \approx 42$ MeV (see Fig. 20.8).

SOLUTION 20.7

The probability amplitude is

$$\langle\phi_f\,|\,\psi_i\rangle = \frac{\langle\phi_f\,|\,E_f - E_i\,|\,\psi_i\rangle}{E_f - E_i} = \frac{\langle\phi_f\,|\,H_1 - H_0\,|\,\psi_i\rangle}{E_f - E_i}$$

If $V = H_1 - H_0$ is small, we may replace $\langle\phi_f|$ by $\langle\psi_f|$ so that

$$|\langle\phi_f\,|\,\psi_i\rangle|^2 \approx \frac{|V_{fi}|^2}{\hbar^2\omega_{fi}^2}$$

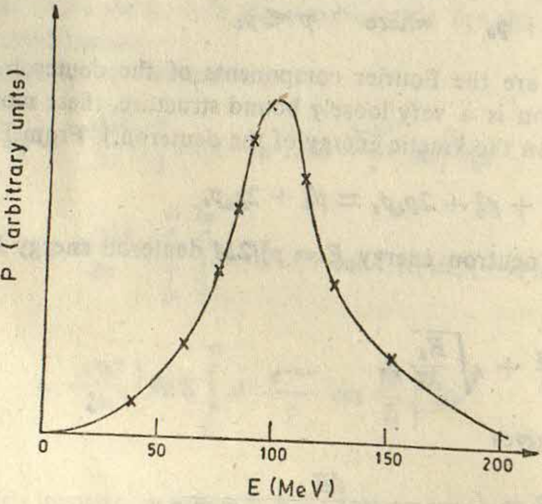

Fig. 20.8 The variation of $P(E)$ with E

SOLUTION 20.8

That the sudden approximation holds may be seen on comparing the beta energy with the atomic binding energies. The change of the nuclear charge and hence the potential, occurs in approximately the time that the beta particle leaves the atom. This time is of the order of $10^{-8}/\frac{1}{3}\, C \sim 10^{-18}$ s; $\omega \sim 10^{17}\ \mathrm{s}^{-1}$ so that $\omega\tau \sim 0.1$. The initial wavefunction is

$$Y_{00}\, R_{10}(Z = 1) = \frac{1}{\sqrt{4\pi}} \left(\frac{1}{a_0}\right)^{3/2} 2e^{-r/a_0}$$

The final wavefunction is

$$Y_{00}\, R_{10}(Z = 2) = \frac{1}{\sqrt{4\pi}} \left(\frac{2}{a_0}\right)^{3/2} 2e^{-2r/a_0}$$

The probability is

$$P = |\int Y_{00}^{*} R_{10}^{*}\, (Z = 2)\, Y_{00}\, R_{10}\, (Z = 1)\, d\tau\, |^2$$

The integral is

$$\frac{2^{3/2}\, 4}{a_0^3} \int\limits_0^\infty e^{-3r/a_0}\, r^2 dr = \frac{2^{3/2}\, 4}{a_0^3}\, \frac{2!}{(3/a_0)^3}$$

or

$$P = (\tfrac{8}{9})^3 \approx 0.703$$

SOLUTION 20.9

The perturbation is

$$V = -\,eE_z \qquad \text{(assuming } E \text{ is along } z\text{)}$$

i.e.

$$V = -\,eE_r \cos\theta \tag{111}$$

The transition probability is

$$|\, C_{n0}\, |^2 = \frac{1}{\hbar^2} \left| \int\limits_{-\infty}^{\infty} \langle n \mid V \mid 0 \rangle\, e^{i\omega t}\, dt \right|^2 \tag{112}$$

where $|\, 0\rangle$ is the ground state; from Eq. (111) it is obvious that there are no transitions to the states $m = \pm 1$ of $2P$. The matrix element $\langle 210 \mid r\cos\theta \mid 100\rangle$ is easily evaluated as $(2^7\sqrt{2}\, a_0/3^5)$. This gives

$$|\, C\, |^2 = \frac{1}{\hbar^2}\, \frac{2^{15}}{3^{10}}\, e^2 a_0^2\, E_0^2\, \frac{\tau^2}{\pi^2} \left| \int\limits_{-\infty}^{\infty} \frac{e^{i\omega t}}{\tau^2 + t^2}\, dt \right|^2$$

The integral can be evaluated by going to the complex t plane on which poles occur at $t = \pm i\tau$. Choosing the contour as the real axis (Fig. 20.9) closed by

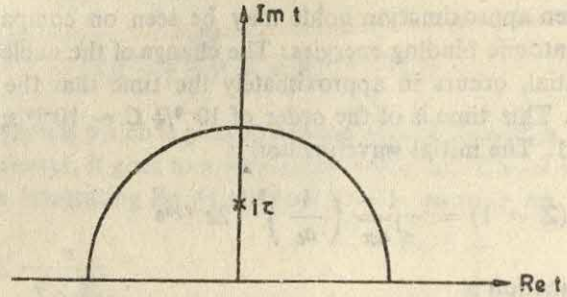

Fig. 20.9 The contour of integration

the upper half semicircle, it is easy to check that the contribution over the semicircle vanishes. Thus

$$\int_{-\infty}^{\infty} \frac{e^{i\omega t}}{t^2 + \tau^2}\, dt = 2i\pi \left(\frac{(t - i\tau)\, e^{i\omega\tau}}{t^2 + \tau^2} \right)_{t = i\tau} = \frac{\pi}{\tau}\, e^{-\omega\tau}$$

Thus the probability is

$$|C|^2 = \frac{1}{\hbar^2}\, \frac{2^{15}}{3^{10}}\, e^2 a_0^2 E_0^2\, e^{-2\omega\tau}$$

The limit $\tau \to \infty$ corresponds to a turning on the perturbation slowly, i.e., $\omega\tau \gg 1$, when the transition probability vanishes. The other limit $\omega\tau \to 0$ corresponds to the application of an impulsive perturbation, with

$$\underset{\tau \to 0}{\mathrm{Lt}}\ \frac{\tau}{\pi(t^2 + \tau^2)} = \delta(t)$$

Solution 20.10

Since $|\, n \rangle$ form a complete set, we may write

$$|\, \Psi(t) \rangle = \sum_n C_n(t)\, |\, n \rangle$$

If we substitute the above expression in the Schrödinger equation

$$i\hbar\, \frac{\partial}{\partial t}\, |\, \Psi(t) \rangle = H\, |\, \Psi \rangle$$

and operate by $\langle m\, |$, we would get Eq. (64).

SOLUTION 20.11

Using Eq. (64) we have the relations

$$i\hbar \frac{\partial C_1}{\partial t} = E_0 C_1 - A C_2$$

$$i\hbar \frac{\partial C_2}{\partial t} = -AC_1 + E_0 C_2$$

These equations are easily solved by forming the linear combinations $C_1 \pm C_2$ so that

$$C_1 + C_2 = C \exp\left[-\frac{i}{\hbar}(E_0 - A)t\right] \tag{113}$$

$$C_1 - C_2 = C' \exp\left[-\frac{i}{\hbar}(E_0 + A)t\right] \tag{114}$$

where C, C' are constants. If it is known that at $t = 0$ the system is in the state $|1\rangle$, we can solve these equations to give

$$C_1(t) = \exp\left(-\frac{i}{\hbar}E_0 t\right)\cos\frac{At}{\hbar}$$

$$C_2(t) = i\exp\left(-\frac{i}{\hbar}E_0 t\right)\sin\frac{At}{\hbar}$$

Thus the time averages $\overline{|C_1(t)|^2}$ and $\overline{|C_2(t)|^2}$ are the same. The energy eigenvalues can also be determined by diagonalizing the Hamiltonian matrix

$$\begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix} \tag{115}$$

This gives

$$(E_0 - \lambda)^2 - A^2 = 0$$

or

$$\lambda = E_0 \mp A \tag{116}$$

This, of course, agrees with Eqs. (113) and (114). The eigenstates are

$$\frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle) = |\psi_\pm\rangle$$

as can be checked by calculating the energies

$$\langle \psi_\pm | H | \psi_\pm \rangle = E_0 \mp A$$

Solution 20.12

Instead of Eq. (116), the Hamiltonian matrix is

$$\begin{pmatrix} E_0 + \mu\varepsilon & -A \\ -A & E_0 - \mu\varepsilon \end{pmatrix}$$

which gives

$$\lambda = E_0 \pm [A^2 + \mu^2\varepsilon^2]^{1/2} \tag{117}$$

For $\mu\varepsilon \ll A$ (which is indeed the case for laboratory electric fields) the energy values of the two states are approximately given by

$$\lambda_{\text{I, II}} = E_0 \pm \left[A + \frac{\mu^2\varepsilon^2}{2A} \right]$$

where I and II refer to the upper and lower energy states. Now, if a collimated beam of ammonia molecules is passed through an inhomogeneous electric field whose gradient is in a direction perpendicular to the beam then the force acting on the molecules in the lower state will be opposite in direction to the force acting on the molecules which are in the upper state. Thus the two molecular states can be separated by passing through an inhomogenous electric field. The molecules in the upper state are then passed through a resonant cavity whose resonance frequency ω_0 equals $2A/\hbar$, then for particular lengths of the cavity all the ammonia molecules (as they pass through the cavity) will make transition to the lower state and thereby emitting electromagnetic waves at the resonant frequency. It should be mentioned that if the two states were not separated then the molecules in the lower state would have taken the energy from the cavity and made transition to the upper state. This is nothing but the condition for 'population inversion' which is necessary for the operation of laser or maser. For more details about the working of the maser, the reader is referred to Feynman (1965) and also to the Nobel lecture of Townes* [reprinted in the book by Thyagarajan and Ghatak (1981)].

Solution 20.13

Since $|\Psi(0)\rangle = |K^0\rangle$, $C_1 = C_2 = 1/\sqrt{2}$; thus

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} (|K^0\rangle + |\bar{K}^0\rangle) \exp(-iE_1 t/\hbar) \exp(-t/2\tau) + \frac{1}{\sqrt{2}} (|K^0\rangle - |\bar{K}^0\rangle) \exp(-iE_2 t/\hbar) \right] \tag{118}$$

Thus the probability that starting from a K^0 particle at $t = 0$ we end up with

---

*C.H. Townes (along with Basov and Prochorov) was awarded the 1964 Nobel prize for Physics for his fundamental work relating to the maser-laser principle.

$\bar{K}^0$ particle at time t is given by

$$|C|^2 = |\langle \bar{K^0} | \Psi(t) \rangle|^2 = \tfrac{1}{4}[1 + e^{-t/\tau_1} - 2e^{-t/2\tau_1} \cos (E_2 - E_1)t/\hbar] \tag{119}$$

If the particles are at rest, then $E_2 - E_1 = C^2 \,\Delta m$ where Δm is the mass difference of K_1^0 and K_2^0. In Eq. (119) if we substitute

$$E_2 - E_1 \approx C^2 \,\Delta m \tag{120}$$

then the mass difference can be determined from the variation of $|C|^2$ with time (see Fig. 20.10).

The behaviour of the neutral K is analogous to that of polarized light. To see this, we first summarize the results of this problem. First, at production the neutral K, produced in strong interactions, is in the state K^0. As time passes by, the K^0 which, according to Eqs. (65) and (66), is an equal mixture of K_1^0 and K_2^0 decays; but it is only the K_1^0 part that decays—the K_2^0 has a long lifetime. The residue, which is practically pure K_2^0 is, according to Eqs. (65) and (66), again a mixture of K^0 and $\bar{K}^0$. We can detect either component by setting up an appropriate detector. In this case, the difference in the behaviour of K^0 and $\bar{K}^0$ is in their strong interactions, and we therefore study a strong reaction induced by the neutral K.

One can construct an analogy identifying the K^0 and $\bar{K}^0$ with the two plane polarized beams of light, one of which is selected by a polarizer. The K_1^0 and K_2^0 then correspond to right and left circularly polarized light, with an absorber which selectively absorbs only the right circularly polarized light.

Returning to Eq. (119), if we substitute experimental values we find

$$\frac{E_2 - E_1}{\hbar} \approx \frac{1}{2\tau_1}$$

Thus

$$|C|^2 \approx \tfrac{1}{4}[1 + e^{-t/\tau_1} - 2e^{-t/2\tau_1} \cos (t/2\tau_1)] \tag{121}$$

The time dependence of $|C|^2$ is shown in Fig. 20.10 which is in agreement with

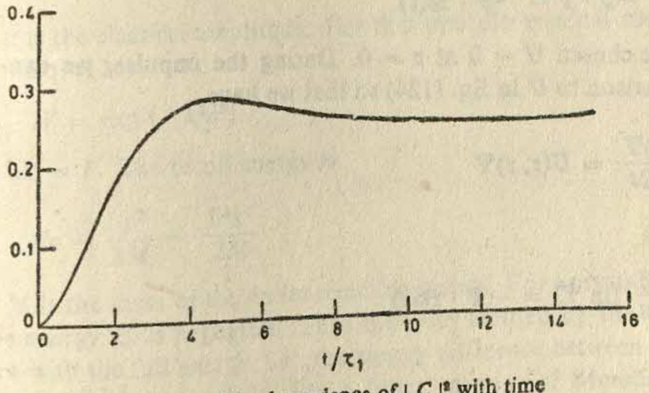

Fig. 20.10 The dependence of $|C|^2$ with time

experimental data. Experimentally, since K^0 and $\bar{K}^0$ are both uncharged particles they leave no tracks; they are distinguished from the fact that K^0 does not interact with matter (except elastically) whereas $\bar{K}^0$ can interact with proton to produce Λ^0 and π^+

$$\bar{K}^0 + p \rightarrow \Lambda^0 + \pi^+ \tag{122}$$

Now in a hydrogen bubble chamber, K^0 is produced through the following reaction

$$\pi^- + p \rightarrow \Lambda^0 + K^0 \tag{123}$$

The trajectory of Λ^0 can be inferred from its subsequent decay to $\pi^- + p$ because both π^- and proton leave tracks. When K^0 is produced in the bubble chamber (see Eq. 123) both K_1^0 and K_2^0 are created [see Eqs. (65) and (66)]; however, K_1^0 decays very quickly (either to $\pi^+ + \pi^-$ or $\pi^0 + \pi^0$). K_2^0 has a large $\bar{K}^0$ component and the $\bar{K}^0$ interacts with hydrogen through the reaction given by Eq. (122). Indeed analysis of the experiment allows one to determine the mass difference. We conclude this problem by noting that conversion of K^0 to $\bar{K}^0$ is a beautiful demonstration of quantum interference effects.

SOLUTION 20.14

(a) The Schrödinger equation for the particle is

$$i\hbar \frac{\partial \Psi}{\partial t} = (T + V + U)\,\Psi \tag{124}$$

where T, V are the kinetic and potential energy operators without the impulse and U represents the energy operator due to the impulse;

$$-\nabla U = \mathbf{F}(t)$$

Integrating, we obtain

$$U = -\mathbf{F} \cdot \mathbf{r} = -\mathbf{P} \cdot \mathbf{r}\delta(t)$$

where we have chosen $U = 0$ at $\mathbf{r} = 0$. During the impulse, we can neglect T, V in comparison to U in Eq. (124) so that we have

$$i\hbar \frac{\partial \Psi}{\partial t} = U(\mathbf{r}, t)\Psi$$

or

$$i\hbar \frac{\partial}{\partial t}\,[\ln \Psi] = -\mathbf{P} \cdot \mathbf{r}\delta(t)$$

Integrating,

$$i\hbar \ln\left(\frac{\Psi_f}{\Psi_i}\right) = -\mathbf{P} \cdot \mathbf{r}$$

or

$$\Psi_f(\mathbf{r}) = \Psi_i(\mathbf{r}) \exp\left[\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{r}\right] \tag{125}$$

(b) The final state given by Eq. (125) is not one of the eigenstates of the system.

We can expand Ψ_f in terms of these eigenstates $\Psi_n(\mathbf{r})$

$$\Psi_f = \Psi_i \exp\left[\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{r}\right] = \sum_n C_n \Psi_n(\mathbf{r})$$

Since Ψ_i, Ψ_n are eigenstates, we can use orthonormality to obtain the coefficients

$$C_n = \int \Psi_n^*(\mathbf{r})\, \Psi_i(\mathbf{r}) \exp\left[\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{r}\right] d^3r$$

$|C_n|^2$ is the probability that the system is in the eigenstate n after the impulse. The above results have a ready application for the so called 'Mossbauer effect'. Here, the nucleus of an atom in a crystal lattice emits a γ-ray, thus delivering an impulse to the crystal. If the crystal is originally in the ground state of its vibrational modes, we can calculate, as above, the probability that it remains in the ground state after the γ-emission. In this situation, it is not the atom, which emits the γ, which will vibrate (since this will leave the crystal in a different state) but the crystal as a whole will recoil without changing its internal state. The probability

$$W = |C_i|^2 = \int \Psi_i^* \exp\left[\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{r}\right] \Psi_i \, d^3r \tag{126}$$

for such an emission is called the Debye-Waller factor. If the system we are considering is, for example, a linear harmonic oscillator, the ground state is

$$\Psi_0(x) = \frac{1}{(\sqrt{\pi a})^{1/2}} \exp\left(-\frac{x^2}{2a^2}\right)$$

where a is the classical amplitude. For this one dimensional case we have, in place of Eq. (126)

$$W = \exp(-k^2a^2) \tag{127}$$

where $\hbar k = P$. The recoil energy is

$$E_R = \frac{p^2}{2M} = \frac{\hbar^2 k^2}{2M}$$

where M is the mass of the entire recoiling system. For a crystal, M is very large and the energy E_R is negligible. Thus the γ-ray emitted by the excited nucleus appears with the full energy, i.e., the energy difference between the excited and ground states of the nucleus. For a fuller account of Mossbauer effect, the reader is referred to Lamb (1960).

SOLUTION 20.14

We have the two reactions

$$A + a \rightarrow B + b \tag{128}$$

and

$$B + b \rightarrow A + a \tag{129}$$

We assume that the matrix element for the processes

$$(\mathbf{p}_A, \mathbf{p}_a, \mathbf{s}_A, \mathbf{s}_a) \rightarrow (\mathbf{p}_B, \mathbf{p}_b, \mathbf{s}_B, \mathbf{s}_b)$$

and

$$(-\mathbf{p}_B, -\mathbf{p}_b, -\mathbf{s}_B, -\mathbf{s}_b) \rightarrow (-\mathbf{p}_A, -\mathbf{p}_a, -\mathbf{s}_A, -\mathbf{s}_a)$$

are the same (this is referred to as the invariance under time reversal). We further assume that the initial beams are unpolarized so that in calculating the cross-section we must sum over the final spin states and average over the initial spin states. Thus, for the reaction given by Eq. (128), instead of $|V|^2$ in Eq. (24) we must have

$$\frac{1}{(2S_A + 1)(2S_a + 1)} \sum |V|^2$$

where the summation is over all the spin states. Similarly, for the reaction given by Eq. (129) we must have

$$\frac{1}{(2S_B + 1)(2S_b + 1)} \sum |V|^2$$

We next calculate the density of states. The number of states with magnitude of momentum lying between p and $p + dp$ is given by (see Eq. 8 of Appendix P)

$$dn = \frac{4\pi p^2\, dp\, V}{(2\pi\hbar)^3} \tag{130}$$

or

$$\frac{dn}{dp} = \frac{Vp^2}{2\pi^2\hbar^3}$$

For the reaction given by Eq. (128) $p = |\mathbf{p}_B| = |\mathbf{p}_b|$ and if E_B and E_b

represent the total particle energies then*

$$\frac{dE}{dp} = \frac{dE_B}{dp} + \frac{dE_b}{dp} = v_{Bb}$$

where v_{Bb} is the relative velocity in the final state. Thus the density of states is given by

$$\frac{dn}{dE} = \frac{Vp^2}{2\pi^2\hbar^3 v_{Bb}} \tag{131}$$

Substituting in the expression for the cross-section [Eq. (43)] and using Eq. (131) we get

$$\sigma_{A+a\to B+b} \propto \frac{|p_B|^2 V}{v_{aA}\, v_{bB}} \frac{1}{(2S_A+1)(2S_a+1)} \sum |V|^2 \tag{132}$$

Similarly

$$\sigma_{B+b\to A+a} \propto \frac{|p_A|^2 V}{v_{bB}\, v_{aA}} \frac{1}{(2S_B+1)(2S_b+1)} \sum |V|^2 \tag{133}$$

(we are assuming the same centre of mass energies). Thus

$$\frac{\sigma_{A+a\to B+b}}{\sigma_{B+b\to A+a}} = \frac{|p_B|^2}{|p_A|^2} \frac{(2S_B+1)(2S_b+1)}{(2S_A+1)(2S_a+1)} \tag{134}$$

where $|\mathbf{p}_A|$ $(= |\mathbf{p}_a|)$ refers to the reaction given by Eq. (129).

SOLUTION 20.15

Using the results of the previous problem we get (at any scattering angle θ)

$$\sigma_{pp\to\pi+d} = \sigma_{\pi+d\to pp} \frac{3}{4}(2S_\pi+1)\left(\frac{p_\pi}{p_p}\right)^2 \tag{135}$$

where we have used the facts that $S_d = 1$ and $S_p = \frac{1}{2}$. If we integrate over

$$E^2 = c^2p^2 + m^2c^4$$

Therefore

$$E\frac{dE}{dp} = c^2p$$

or

$$\frac{dE}{dp} = \frac{c^2p}{E} = \frac{c^2(m_0v\gamma)}{(m_0c^2\gamma)} = v$$

where

$$\gamma = \left(1 - \frac{v^2}{c^2}\right)^{-1/2}$$

all angles, we must multiply by a factor of two to take into account the indistinguishability of protons in the final state of the $\pi^+ d \to pp$ reaction. Then

$$\sigma_{pp\to\pi^+d} = \sigma_{\pi^+d\to pp}\,\frac{3}{2}\,(2s_\pi + 1)\left(\frac{p_\pi}{p_p}\right)^2 \tag{136}$$

SOLUTION 20.16

In the experiment of Cartwright *et al.*, the incident proton energy of 340 MeV corresponds to a meson energy of 22.3 MeV in the c.m.s. (see Sec. 19.8). On the other hand, in the experiment of Durbin *et al.*, the incident meson energy of 29 MeV corresponds to meson energy of 25 MeV in the c.m.s. Thus both the experiments correspond approximately to the same centre of mass energies. Further, since the energies involved are small compared to the rest mass energies, we may use the non-relativistic expressions giving

$$\frac{p_\pi}{p_p} = \sqrt{\frac{2m_\pi\, E_\pi}{2m_p\, E_p}} \approx 0.20$$

Substituting in Eq. (136) we get

$$(0.18 \pm 0.06) = (3.1 \pm 0.3) \times 1.5 \times 0.04 \times (2s_\pi + 1)$$

giving

$$2s_\pi + 1 \approx 1$$

or the spin of the π meson is zero. For further details on the spin and parity of elementary particles see Hughes (1972).

SOLUTION 20.17

This problem is really an exercise in the calculation of the density of states. Let E be the rest energy of the K^+. We then have the constraints :

$$\begin{aligned} E &= \epsilon_1 + \epsilon_2 + \epsilon_3 \\ 0 &= \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 \end{aligned} \tag{137}$$

Let us assume that $\mathbf{p}_1$ is held fixed. We now calculate the number of final states with this constraint. (Throughout these calculations we shall use the simple rule that the number of states is $1/(2\pi\hbar)^3 \times$ phase volume.)

We are interested in the number of states dN such that the energies of two of the pions are fixed, within infinitesimal intervals, and the remaining parameter varied. If we fix $\mathbf{p}_1$ and $\mathbf{p}_2$, it is clear that energy conservation will automatically fix the magnitude of $\mathbf{p}_3$ (see Fig. 20.11). Looking at the diagram, we see that this also fixes θ_2. Now the number dN is

$$dN = \frac{p_1^2\, dp_1\, d\Omega_1}{(2\pi\hbar)^3}\,\frac{p_2^2\, dp_2\, d\Omega_2}{(2\pi\hbar)^3}\,V^2 \tag{138}$$

volume of the box in which the event takes place and $d\Omega_1$ and ngle intervals within which $\mathbf{p}_1$ and $\mathbf{p}_2$ lie. Once we consider $\mathbf{p}_1$, erely have to count dN as the number of states within the energy

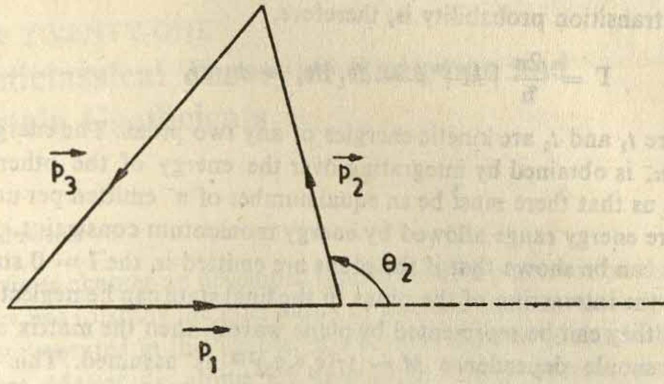

Fig. 20.11

interval dE, a variation which is related directly to the interval $(d\Omega_2)$. To get this relation we use momentum conservation

$$p_1^2 + p_2^2 + 2p_1 p_2 \cos\theta_2 = p_3^2 \tag{139}$$

Since $p_i^2 + m_i^2 = \epsilon_i^2$ (we have used $c = 1$) we can write Eq. (139) as

$$p_1^2 + p_2^2 + 2\, p_1\, p_2 \cos\theta_2 = \epsilon_3^2 - m_3^2$$

or

$$p_1^2 + p_2^2 + 2p_1\, p_2 \cos\theta_2 = (E - \epsilon_1 - \epsilon_2)^2 - m_3^2 \tag{140}$$

Since we keep $p_1, p_2, \epsilon_1, \epsilon_2$ fixed, we get

$$2p_1\, p_2\, d\,(\cos\theta_2) = 2\,(E - \epsilon_1 - \epsilon_2)\, dE = 2\epsilon_3\, dE$$

or

$$d\,(\cos\theta_2) = \frac{\epsilon_3 dE}{p_1\, p_2} \tag{141}$$

The orientation ϕ_2 in $d\Omega_2$ is irrelevant so we can integrate over it. Moreover, we can now also integrate over $d\Omega_1$, since no further constraint is involved. This gives

$$dN = \frac{4\pi\cdot 2\pi}{(2\pi\hbar)^6}\, p_1\, dp_1\, p_2\, dp_2\, \epsilon_3\, dE\, V^2 \tag{142}$$

Since $p_i\, dp_i = \epsilon_i\, d\epsilon_i$, we have finally (inserting the factor c which we had dropped)

$$\rho = \frac{dN}{dE} = \frac{8\pi^2 V^2}{(2\pi\hbar)^6 c^6}\, \epsilon_1 \epsilon_2 \epsilon_3\, d\epsilon_1 d\epsilon_2 \tag{143}$$

The transition probability is, therefore,

$$\Gamma = \frac{2\pi}{\hbar} | M |^2 \rho \sim d\epsilon_1 \, d\epsilon_2 = dt_1 \, dt_2 \tag{144}$$

where t_1 and t_2 are kinetic energies of any two pions. The energy distribution of the π^- is obtained by integrating over the energy of the other. But Eq. (144) tells us that there must be an equal number of π^- emitted per unit energy for the entire energy range allowed by energy momentum constraint.

It can be shown that if the pions are emitted in the $l = 0$ state (low energy) and the interaction of the pions in the final state can be neglected (which means that they can be represented by plane waves), then the matrix element will have the simple dependence $M \sim 1/(\epsilon_1\epsilon_2\epsilon_3)^{1/2}$ as assumed. This means that any deviation from the prediction (144), which can be called the 'phase space spectrum', may be attributed to some interaction of the pions in the final state. In the extreme case where two of the pions really are the products of the *decay* of a particle which emerged from the original reaction, there would be a very strong deviation from the phase space spectrum. As an example, we may have

$$\begin{array}{l} \pi^+ + d \rightarrow \omega + p + p \\ \quad\;\; \lfloor\!\!\rightarrow (\pi^+ + \pi^- + \pi^0) \end{array}$$

In a bubble chamber, only the three pions are seen but from their energy spectrum one can infer the existence and properties of ω. A very shortlived particle such as the ω is sometimes referred to as a resonance.

CHAPTER TWENTY-ONE

The Semiclassical Theory of Radiation and the Einstein Coefficients

21.1 Introduction

In the previous chapter we developed time-dependent perturbation theory which we will now use to study the interaction of an atom with electromagnetic field. The theory presented in this chapter is a curious mixture of classical and quantum pictures. Matter, i.e. atoms, are assumed to exist in discrete (quasi-stationary) states. But the electromagnetic radiation with which it interacts, is described classically. This semiclassical theory of atom-field interaction will be discussed in Sec. 21.3 which will enable us to calculate probabilities of absorption and induced emission. It may be mentioned that the semiclassical theory is insufficient to describe the spontaneous emission of radiation because the electromagnetic field is described classically; the fully quantum theory, which we will discuss in the next chapter, describes the spontaneous emission automatically.

An ingenious idea of Einstein enabled him to obtain a relation which would determine the rate at which spontaneous emissions take place. The idea was based on consideration of matter in equilibrium with radiation assuming that the resultant radiation must obey Planck's law. Einstein introduced coefficients, which are now known as Einstein coefficients, which described induced emission, absorption and spontaneous emission. In Sec. 21.2 we will give the original argument of Einstein (1917) which gave rise to the relation between different coefficients. In Sec. 21.3 we will discuss the atom-field interaction using the semiclassical theory and will derive expressions for stimulated emission rate and stimulated absorption rate. In Sec. 21.4 we will use the Einstein relations to calculate the spontaneous emission rate and hence the life time of atomic states. In Sec. 21.5, we will discuss the selection rules governing the transitions.

21.2 The Einstein Coefficients

Figure 21.1 represents two of the energy levels of an atomic system corresponding to energies E_1 and E_2. Let N_1 and N_2 represent the number of atoms (per unit volume) in levels 1 and 2 respectively. An atom in the lower energy level can absorb radiation and get excited to the level E_2. This excitation process can

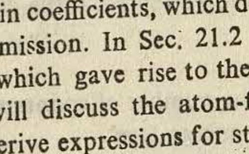

Fig. 21.1 The two states of an atomic system. The transition frequency is $\omega_{21} = (E_2 - E_1)/\hbar$.

occur only in the presence of radiation. Such a process is known as stimulated absorption or simply absorption. The rate of absorption would depend on the energy density, $u(\omega)$, associated with the radiation field corresponding to the frequency

$$\omega = \frac{E_2 - E_1}{\hbar} \tag{1}$$

The energy density $u(\omega)$ is defined such that $u(\omega)\, d\omega$ represents the radiation energy per unit volume within the frequency interval ω and $\omega + d\omega$. The rate of absorption would be proportional to N_1 and also to $u(\omega)$. Thus, the number of absorptions per unit time per unit volume can be written as

$$N_1 B_{12}\, u(\omega) \tag{2}$$

where B_{12} is the coefficient of proportionality and is a characteristic of the energy levels.

On the other hand, when the atom is in an excited state, it can make a transition to a lower energy state through the emission of electromagnetic radiation; however, in contrast to the absorption process, the emission process can occur in two different ways:

The first is referred to as spontaneous emission in which an atom in the excited state emits radiation even in the absence of any incident radiation. It is thus not stimulated by any incident signal but occurs spontaneously. Further, the rate of spontaneous emissions is proportional to the number of atoms in the excited state; thus if we represent the coefficient of proportionality by A_{21} then

$$N_2 A_{21} \tag{3}$$

would represent the number of spontaneous emissions per unit volume per unit time to the lower energy level.

The second is referred to as stimulated emission in which an incident signal of appropriate frequency triggers an atom in an excited state to emit radiation. The rate of transition to the lower energy level is directly proportional to the energy density of the radiation at the frequency ω. Thus the number of stimulated emissions per unit time per unit volume would be given by

$$N_2 B_{21}\, u(\omega) \tag{4}$$

The quantities A_{21}, B_{12} and B_{21} are known as Einstein coefficients and are determined by the atomic system.

At thermal equilibrium, the number of upward transitions must be equal to the number of downward transitions. Thus, we may write

$$N_1 B_{12}\, u(\omega) = N_2 A_{21} + N_2 B_{21}\, u(\omega)$$

or

$$u(\omega) = \frac{A_{21}}{(N_1/N_2)\,(B_{12} - B_{21})} \tag{5}$$

From Boltzmann's law, we have the following expression for the ratio of the populations of two levels at temperature T:

$$\frac{N_1}{N_2} = \exp\left[\frac{E_2 - E_1}{k_B T}\right] = \exp\left[\frac{\hbar\omega}{k_B T}\right] \tag{6}$$

where k_B represents the Boltzmann constant. Thus, we may write

$$u(\omega) = \frac{A_{21}}{B_{12}\exp(\hbar\omega/k_B T) - B_{21}} \tag{7}$$

Now, according to Planck's law the energy density of radiation (at thermal equilibrium) is given by (see, e.g., Thyagarajan and Ghatak, 1981):

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\,\frac{1}{\exp(\hbar\omega/k_B T) - 1} \tag{8}$$

Comparing Eqs. (7) and (8) we obtain*

$$B_{12} = B_{21} = B \text{ (say)} \tag{9}$$

and

$$\frac{A_{21}}{B_{21}} = \frac{\hbar\omega^3}{\pi^2 c^3} \tag{10}$$

Thus, the probabilities of stimulated absorption and stimulated emission are the same and the ratio of the A and B coefficients is given by Eq. (10). It is of interest to mention that at thermal equilibrium corresponding to ordinary temperatures ($T \sim 1000$°K) the spontaneous emission rate for optical sources far exceeds the stimulated emission rate (see Problem 21.1).

21.3 The Atom-Field Interaction

In order to calculate the Einstein coefficients we consider an atom in the presence of an oscillating electric field given by**

$$\mathcal{E}(t) = \hat{e}\,\mathcal{E}_0 \cos\omega t \tag{11}$$

which is switched on at $t = 0$; $\hat{e}$ represents the unit vector along the direction of the electric field and the oscillation frequency ω is assumed to be close to the resonant frequency ω_{21} $[= (E_2 - E_1)/\hbar]$ corresponding to the transition from state 2 to state 1 (see Fig. 21.1). Now, the interaction energy of the electron with the electric field is given by

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*If the levels 1 and 2 are g_1 and g_2-fold degenerate, then $N_1/N_2 = (g_1/g_2)\exp(\hbar\omega/k_B T)$, $B_{12} = B_{21}(g_2/g_1)$ and $A_{21}/B_{21} = \hbar\omega^3/\pi^2 c^3$.

**The electric field associated with an electromagnetic wave will be of the form $\hat{e}\cos(\omega t - \mathbf{k}\cdot\mathbf{r})$; however, for radiation in the visible region, the wavelength associated ($\sim 5 \times 10^{-5}$ cm) is much larger than atomic dimensions ($\sim 10^{-8}$ cm) and we can use the value of $\mathcal{E}$ at $\mathbf{r} = 0$. This is immediately obvious from Eq. (17) where the atomic wavefunctions are almost zero for $\mathbf{r} \gtrsim 10^{-8}$ cm and since $k \simeq 10^5$ cm^{-1}, the quantity $\mathbf{k}\cdot\mathbf{r} \ll 1$ in the domain of integration.

$$H'(\mathbf{r}, t) = q\,\mathcal{E} \cdot \mathbf{r} = q\mathcal{E}_0(\hat{\mathbf{e}} \cdot \mathbf{r}) \cos \omega t \tag{12}$$

where $q(> 0)$ represents the magnitude of the electronic charge*. Let H_0 represent the Hamiltonian corresponding to the atomic system and let ψ_n denote the eigenfunctions of H_0 belonging to the energy E_n $(= \hbar\omega_n)$:

$$H_0\psi_n = E_n\psi_n = \hbar\omega_n\,\psi_n \tag{13}$$

Our objective is to solve the equation

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = H\Psi = [H_0 + H'(\mathbf{r}, t)]\,\Psi(\mathbf{r}, t) \tag{14}$$

Following the approach developed in Sec. 20.2, we write

$$\Psi(\mathbf{r}, t) = \sum_n C_n(t)\, e^{-i\omega_n t}\, \psi_n(\mathbf{r}) \tag{15}$$

and obtain [see Eq. (9) of the previous chapter]

$$i\hbar \frac{dC_s}{dt} = \sum C_n(t) H'_{sn}(t)\, e^{i\omega_{sn}t} \tag{16}$$

where

$$\begin{aligned} H'_{sn}(t) &= \int \psi_s^*(\mathbf{r})\, H'(\mathbf{r}, t)\, \psi_n(\mathbf{r})\, d\mathbf{r} = \langle s \mid H' \mid n \rangle \\ &= \tfrac{1}{2}\, q\mathcal{E}_0\, \hat{\mathbf{e}} \cdot \langle s \mid \mathbf{r} \mid n \rangle\, [e^{i\omega t} + e^{-i\omega t}] \end{aligned} \tag{17}$$

Substituting for $H'(\mathbf{r}, t)$ from Eq. (12), we get

$$i\hbar \frac{dC_s}{dt} = \frac{1}{2}\,\mathcal{E}_0 \sum_n \mathcal{D}_{sn}\, C_n(t)\, [e^{i(\omega_{sn}+\omega)t} + e^{i(\omega_{sn}-\omega)t}] \tag{18}$$

where

$$\mathcal{D}_{sn} = \hat{\mathbf{e}} \cdot \mathbf{P}_{sn} \tag{19}$$

and

$$\mathbf{P}_{sn} = q \int \psi_s^*(\mathbf{r})\, \mathbf{r}\psi_n(\mathbf{r})\, d\mathbf{r} = q\,\langle s \mid \mathbf{r} \mid n \rangle \tag{20}$$

is known as the dipole matrix element. We assume that at $t = 0$ the atom is in the state ψ_k, i.e.,

---

*We are considering here a single electron atom with $\mathbf{r}$ representing the position vector of the electron with respect to the nucleus. Thus the electric dipole moment of the atom is given by $\mathbf{p} = -q\mathbf{r}$ because the direction of the dipole moment is from the negative charge to the positive charge. The interaction energy of a dipole placed in an electric field is $-\mathbf{p} \cdot \mathcal{E}$ which is precisely Eq. (12). It may be mentioned that the interaction term described by Eq. (12) is consistent with the Schrödinger equation for the electron in the dipole approximation (see Sec. 22.4).

$$\left.\begin{aligned} C_k(t=0) &= 1 \\ C_n(t=0) &= 0 \quad \text{for} \quad n \neq k \end{aligned}\right\} \tag{21}$$

Equation (18) represents an infinite set of coupled equations and as a first approximation we replace $C_n(t)$ by $C_n(0)$ on the right hand side of Eq. (18) giving

$$i\hbar \frac{dC_s}{dt} \simeq \frac{1}{2} \mathcal{E}_0 \mathcal{D}_{sk} \left[e^{i(\omega_{sk}+\omega)t} + e^{i(\omega_{sk}-\omega)t}\right]$$

Integrating, we obtain

$$C_s(t) - C_s(0) = -\frac{i\mathcal{E}_0}{2\hbar} \mathcal{D}_{sk} \left[\frac{e^{i(\omega_{sk}+\omega)t} - 1}{i(\omega_{sk}+\omega)} + \frac{e^{i(\omega_{sk}-\omega)t} - 1}{i(\omega_{sk}-\omega)}\right]$$

or, for $s \neq k$

$$\begin{aligned} C_s(t) = -\frac{i\mathcal{E}_0}{2\hbar} \mathcal{D}_{sk} \Bigg[& e^{i(\omega_{sk}+\omega)t/2} \frac{\sin (\omega_{sk}+\omega)t/2}{(\omega_{sk}+\omega)/2} \\ & + e^{i(\omega_{sk}-\omega)t/2} \frac{\sin (\omega_{sk}-\omega)t/2}{(\omega_{sk}-\omega)/2} \Bigg] \end{aligned} \tag{22}$$

It can be easily seen that for large values of t, the function

$$\frac{\sin (\omega_{sk}-\omega)\, t/2}{(\omega_{sk}-\omega)/2} \tag{23}$$

is very sharply peaked around $\omega \simeq \omega_{sk}$ and negligible everywhere else (see Fig. 21.2). Thus for states for which ω_{sk} is significantly different from ω, $C_s(t)$ would

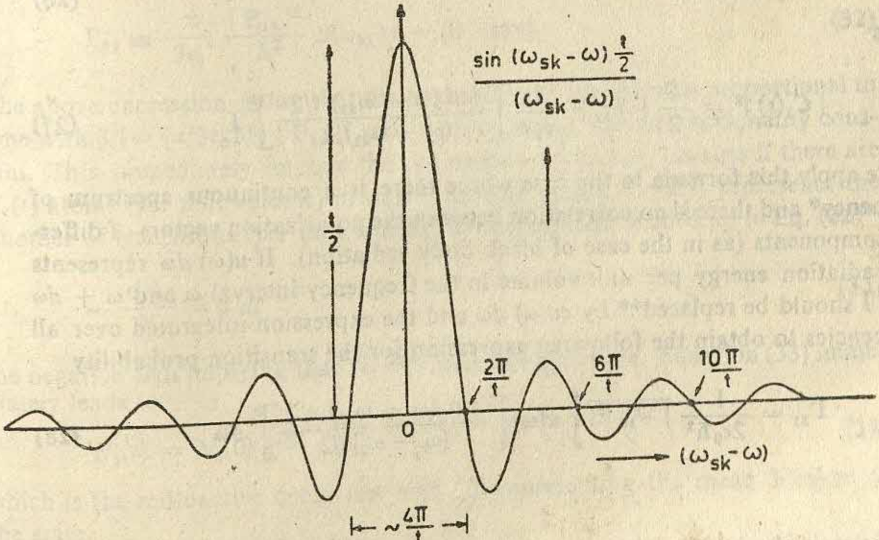

Fig. 21.2 For large values of t, the function given by Eq. (23) is a very sharply peaked function of ω about $\omega = \omega_{sk}$.

be negligible, and transitions between such states will not be stimulated by the incident field. The implies that in the summation appearing on the right hand side of Eq. (18) we need only consider those states which correspond closely to the resonance frequency.

In an emission process, $E_k > E_s$ and hence ω_{sk} $[= (E_s - E_k)/\hbar]$ is negative; thus it is the first term on the right hand side of Eq. (22) which contributes. On the other hand, in an absorption process, $E_k < E_s$ and hence ω_{sk} is positive and consequently it will be the second term on the right hand side of Eq. (22) which contributes.

Let us consider the emission of radiation and assume that at $t = 0$ the atom is in state 2 (see Fig. 21.1). We also assume ω to be close to ω_{21} $[= (E_2 - E_1)/\hbar]$. The probability for the transition to state 1 is given by

$$|C_1(t)|^2 = \frac{|\mathcal{D}_{12}|^2 \mathcal{E}_0^2}{4\hbar^2}\left[\frac{\sin(-\omega_{21}+\omega)\,t/2}{(-\omega_{21}+\omega)/2}\right]^2 \tag{24}$$

Equation (24) represents the probability for stimulated emission of radiation. In deriving this equation, we have assumed that $|C_1(t)|^2 \ll 1$; thus the result will be valid when either

$$\left(\frac{\mathcal{D}_{12}\mathcal{E}_0 t}{\hbar}\right)^2 \ll 1 \quad \text{or} \quad \left(\frac{\mathcal{D}_{12}\mathcal{E}_0}{\hbar}\right)^2 \Big/ (\omega - \omega_{21})^2 \ll 1 \tag{25}$$

A more accurate result for a two state system will be discussed in Problem 21.8.

Now, the intensity of an electromagnetic wave is related to $\mathcal{E}_0^2$ through the relation (see, for example, Ghatak, 1977, Sec. 19.5)

$$I = \tfrac{1}{2}\epsilon_0 c\, \mathcal{E}_0^2 \tag{26}$$

Thus

$$|C_1(t)|^2 = \frac{1}{2}|\mathcal{D}_{12}|^2 \frac{1}{\epsilon_0 c}\left[\frac{\sin(\omega-\omega_{21})\,t/2}{(\omega-\omega_{21})/2}\right]^2 I \tag{27}$$

We apply this formula to the case where there is a continuous spectrum of frequency* and there is no correlation between the polarization vectors of different components (as in the case of black body radiation). If $u(\omega)\,d\omega$ represents the radiation energy per unit volume in the frequency interval ω and $\omega + d\omega$ then I should be replaced** by $cu(\omega)\,d\omega$ and the expression integrated over all frequencies to obtain the following expression for the transition probability

$$\Gamma_{21} = \frac{1}{2\epsilon_0\hbar^2}\overline{|\mathcal{D}_{12}|^2}\int u(\omega)\left[\frac{\sin(\omega-\omega_{21})\,t/2}{(\omega-\omega_{21})/2}\right]^2 d\omega \tag{28}$$

---

*One could also have an interaction of a near monochromatic wave (as in a laser) with an atom having a broad frequency spectrum. This is discussed in Problem 21.10.

**The energy density associated with a monochromatic field is I/c.

where the bar denotes the averaging over different orientations:

$$\overline{|\mathscr{D}_{12}|^2} = q^2 \overline{|\langle 1 | \mathbf{r} | 2\rangle \cdot \hat{\mathbf{e}}|^2} = q^2 |\langle 1 | \mathbf{r} | 2\rangle|^2 \overline{\cos^2 \theta}$$

$$= \frac{q^2}{3} |\langle 1 | \mathbf{r} | 2\rangle|^2 = \frac{1}{3} |\mathbf{P}_{12}|^2$$

because

$$\overline{\cos^2 \theta} = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \cos^2\theta \sin\theta \, d\theta \, d\varphi = \frac{1}{3} \tag{29}$$

Assuming that $u(\omega)$ varies much slowly in comparison to the quantity

$$\left[\frac{\sin (\omega - \omega_{21}) \, t/2}{(\omega - \omega_{21})/2}\right]^2 \tag{30}$$

we replace $u(\omega)$ by its value at $\omega = \omega_{21}$ and take it out of the integral (in Eq. 28) to obtain

$$\Gamma_{21} \simeq \frac{1}{6\epsilon_0 \hbar^2} |\mathbf{P}_{12}|^2 u(\omega_{21}) \, G \tag{31}$$

where

$$G \simeq \int_{-\infty}^{+\infty} \left[\frac{\sin (\omega_{21} - \omega) \, t/2}{(\omega_{21} - \omega)/2}\right]^2 d\omega = 2t \int_{-\infty}^{+\infty} \frac{\sin^2 \xi}{\xi^2} \, d\xi = 2\pi t$$

Thus

$$\Gamma_{21} \simeq \frac{\pi}{3\epsilon_0} \frac{|\mathbf{P}_{12}|^2}{\hbar^2} u(\omega_{21}) \, t = \beta t \text{ (say)} \tag{32}$$

The above expression shows that the probability of transition is proportional to time with $\beta \, [= (\pi/3\epsilon_0\hbar^2) \, |\mathbf{P}_{12}|^2 \, u(\omega_{21})]$ representing the proportionality constant. This immediately implies the radioactive decay law, because if there are $N_2(t)$ atoms (per unit volume) in state 2 at time t and if $-dN_2$ represents the number of transitions (per unit volume) in time dt then according to Eq. (32)*

$$-\frac{dN_2}{N_2} = \beta \, dt \tag{33}$$

the negative sign implying that N_2 will decrease with time. Equation (33) immediately leads to

$$N_2(t) = N_2(0) \, e^{-\beta t} \tag{34}$$

which is the radioactive decay law with $1/\beta$ representing the mean lifetime of the state.

---

*It should be noted that we are not taking into account the increase in the number of atoms in state 2 because of stimulated absorptions. The analysis however remains valid.

It may be noted that Eq. (32) predicts an indefinite increase in the transition probability with time; however, the first order perturbation theory itself breaks down when Γ_{21} is not appreciably less than unity. Thus, Eq. (32) is valid for times for which

$$\beta t \ll 1 \tag{35}$$

If the lifetime of the state is $\sim 10^{-9}$ sec, then $\beta \sim 10^{9}$ sec^{-1} and we must have

$$t \ll 10^{-9} \text{ sec} \tag{36}$$

However, the large time behaviour is given by Eq. (34)*.

It should also be noted that in our analysis we have assumed the quantity given by Eq. (30) to be very sharply peaked around $\omega \approx \omega_{21}$, for this to happen t should be large enough so that**

$$1/t\omega_{21} \ll 1$$

or

$$t \gg 1/\omega_{21} \tag{37}$$

Now in the optical region

$$\omega_{21} \sim 10^{15} \text{ sec}^{-1}$$

then we must have

$$t \gg 10^{-15} \text{ sec}$$

Thus t in Eq. (32) should satisfy Eq. (37).

Returning to Eq. (32), we get the following expression for the transition probability per unit time (which we denote by w_{21})

$$w_{21} \cong \frac{\pi}{3\epsilon_0\hbar^2}\,|\,\mathbf{P}_{12}\,|^2\,u(\omega_{21}) \tag{38}$$

If there are N_2 atoms per unit volume in state 2 then the number of stimulated emissions per unit time per unit volume would be given by

$$W_{21} = N_2\, w_{21} = N_2\,\frac{\pi}{3\epsilon_0\hbar^2}\,|\,\mathbf{P}_{12}\,|^2\,u(\omega_{21}) \tag{39}$$

Comparing the above equation with Eq. (4), we obtain

$$\begin{aligned} B_{21} &= \frac{\pi}{3\epsilon_0}\,\frac{P^2}{\hbar^2} = \frac{4\pi^2}{3\hbar^2}\left(\frac{q^2}{4\pi\epsilon_0}\right)\left|\int \psi_1^*\,\mathbf{r}\,\psi_2\,d\mathbf{r}\right|^2 \text{ (in MKS units)} \\ &= \frac{4\pi^2 e^2}{3\hbar^2}\,|\,\langle\, 1\,|\,\mathbf{r}\,|\,2\,\rangle\,|^2 \text{ (in CGS units)} \end{aligned} \tag{40}$$

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*Equation (32) may therefore be interpreted as : If the state has not made a transition up to time t then the probability that it will make a transition in dt will be $\beta\, dt$ from which Eq. (34) follows.

**This follows from the fact that the maximum of Eq. (30) occurs at $\omega = \omega_{21}$ and the first zero at $(\omega = \omega_{21} \pm \pi/t)$.

where e represents the magnitude of the electronic charge in CGS units.

The corresponding expression for stimulated absorption is obtained by starting with the first term on the right hand side of Eq. (22) and proceeding in a similar manner. The final expression is identical to Eq. (40) except for an interchange of indices 1 and 2 and since

$$|\int \psi_2^* \mathbf{r}\, \psi_1\, d\mathbf{r}\,|^2 = |\int \psi_1^* \mathbf{r}\, \psi_2\, d\mathbf{r}\,|^2 \tag{41}$$

we get

$$B_{12} = B_{21}$$

consistent with Eq. (9).

21.4 Spontaneous Emission Rate

Using Eqs. (9), (10) and (40), we get the following expression for the A coefficient

$$A = \frac{4}{3}\,\alpha\,\frac{\omega^3}{c^2}\left|\int \psi_1^* \mathbf{r}\, \psi_2\, d\tau\right|^2 \tag{42}$$

where

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137} \tag{43}$$

is known as the fine structure constant. For the $2P \to 1S$ transition in the hydrogen atom, i.e., for the transition from any one of the ($n = 2, l = 1, m = +1, 0, -1$) states to the ($n = 1, l = 0, m = 0$) state, we get (see Problem 21.3)

$$\left|\int \psi_{1S}^* \mathbf{r}\, \psi_{2P}\, d\tau\right|^2 = 2^5\left(\frac{2}{3}\right)^{10} a_0^2 \tag{44}$$

independent of the initial value of m. Here a_0 [$= (\hbar^2/me^2) \simeq 0.5 \times 10^{-10}$ m] is the Bohr radius. Further, for $2P \to 1S$ transition

$$\hbar\omega = \left(-\frac{1}{4} + 1\right)E_H = \frac{3}{8}\frac{e^2}{a_0}$$

or

$$\omega = \frac{3c}{8a_0}\,\alpha \tag{45}$$

On substitution in Eq. (42), we get

$$A = \left(\frac{4}{9}\,\alpha\right)^4 \frac{c}{a_0} \simeq 6 \times 10^8\ \text{sec}^{-1}$$

The coefficient A gives the probability per unit time for spontaneous emission from state 2 to state 1. Thus if there are N_2 atoms per unit volume in state 2 and if $-dN_2$ represents the number of atoms undergoing spontaneous transitions in time dt then

$$dN_2 = -AN_2\, dt \tag{46}$$

giving once again the radioactive decay law

$$N_2(t) = N_2(0)\, e^{-At}$$

Thus the mean lifetime of the state is given by

$$\tau = \frac{1}{A} \simeq 1.6 \times 10^{-9} \text{ sec} \tag{47}$$

In Eq. (46), dt should be small enough so that $A\, dt \ll 1$. Equation (47) tells us that the mean lifetime of the hydrogen atom in the upper level corresponding to the $2P \rightarrow 1S$ transition is about 1.6×10^{-9} sec. Transitions having such small lifetimes are referred to as strongly allowed transitions*. One can similarly calculate lifetimes for other atomic states.

The spontaneous emission rate will give rise to finite widths of the spectral lines which can be estimated from the uncertainty principle

$$\Delta E \sim \frac{\hbar}{\tau} \tag{48}$$

In practice, the observed widths are much larger because of other factors such as Doppler broadening, collision broadening, etc.

We should also mention here that the A coefficient for the $2S \rightarrow 1S$ transition is zero. Such transitions are said to be forbidden transitions.

21.5 The Selection Rules

Whenever the quantity

$$\hat{\mathbf{e}} \cdot \int \psi_f^* \mathbf{r}\, \psi_i\, d\tau$$

(also written as $\hat{\mathbf{e}} \cdot \langle f \mid \mathbf{r} \mid i \rangle$) vanishes, the transition probability is zero (see Eq. 24) and the corresponding transition is said to be forbidden (in the dipole approximation)**; the subscripts i and f refer to initial and final states respectively. If we assume that the electron moves in a central field, then the angular

---

*In contrast, the levels used in the laser transition are such that the upper level has a very long lifetime ($\sim 10^{-3}$ to 10^{-5} sec). Such levels are referred to as metastable levels. The strength of an atomic transition is usually expressed in terms of the f-value defined by the equation

$$f = \frac{2}{3} \frac{m\omega_{21}}{\hbar} \mid \mathscr{D}_{21} \mid^2$$

For strongly allowed transitions $f \sim 1$ and for transitions from metastable levels $f \sim 10^{-3} - 10^{-6}$.

**See Problem 22.1 for higher order transitions.

part of the wavefunction will be of the form $Y_{lm}(\theta, \varphi)$; thus the initial and final states will be given by

$$\left.\begin{aligned} \psi_i &= R_{n_i l_i} Y_{l_i m_i}(\theta, \varphi) \\ \text{and} \qquad \psi_f &= R_{n_f l_f} Y_{l_f m_f}(\theta, \varphi) \end{aligned}\right\} \tag{49}$$

Now, it can be shown that (see Problem 21.2)

$$\int \psi_f^* z \psi_i \, d\tau = G\left[\delta_{l_f, l_i+1} \left(\frac{(l_i + m_i + 1)(l_i - m_i + 1)}{(2l_i + 1)(2l_i + 3)} \right)^{1/2} + \delta_{l_f, l_i-1} \left(\frac{(l_i + m_i)(l_i - m_i)}{(2l_i + 1)(2l_i + 3)} \right)^{1/2} \right] \delta_{m_f, m_i} \tag{50}$$

and

$$\int \psi_f^* (x \pm iy) \psi_i \, d\tau = G\left[\delta_{l_f, l_i+1} \left(\frac{(l_i + m_i + 1)(l_i + m_i + 2)}{(2l_i + 1)(2l_i + 3)} \right)^{1/2} \pm \delta_{l_f, l_i-1} \left(\frac{(l_i - m_i)(l_i - m_i - 1)}{(2l_i + 1)(2l_i - 1)} \right)^{1/2} \right] \delta_{m_f, m_i \pm 1} \tag{51}$$

where

$$G = \int_0^\infty r^3 R_{n_f l_f}(r) R_{n_i l_i}(r) \, dr \tag{52}$$

where R_{nl} represents the radial part of the wavefunctions. Equations (50) and (51) tell us that for a transition to occur, we must have

$$\left.\begin{aligned} \Delta l &= l_f - l_i = \pm 1 \\ \Delta m &= m_f - m_i = 0 \end{aligned}\right\} \tag{53}$$

and

$$\left.\begin{aligned} \Delta l &= l_f - l_i = \pm 1 \\ \Delta m &= m_f - m_i = \pm 1 \end{aligned}\right\} \tag{54}$$

which are known as the *selection rules*. Since spin angular momenta are not involved, we have

$$\Delta j = \pm 1 \tag{55}$$

as well.

Now, for the $\Delta m = 0$ transition, the vector

$$\mathbf{P} = q \int \psi_f^* \mathbf{r} \psi_i \, d\tau \tag{56}$$

is along the z-direction (because $P_x = P_y = 0$, see Eq. 51). Since the transition

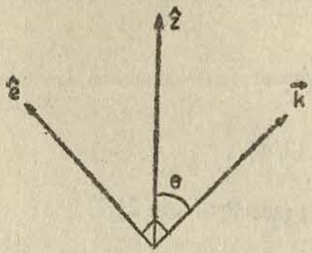

Fig. 21.3 The vector k represents the direction of propagation of the emitted radiation. The plane of the paper is defined by the vectors k and $\hat{\mathbf{z}}$. For the $\Delta m = 0$ transition, the polarization vector of the emitted radiation $\hat{\mathbf{e}}$ will lie in the $\mathbf{k}-\hat{\mathbf{z}}$ plane with the intensity of radiation maximum for $\theta = \pi/2$ and zero for $\theta = 0$.

rate is proportional to*

$$|\mathbf{P}\cdot\hat{\mathbf{e}}|^2 \tag{57}$$

the electric field associated with the emitted radiation will have no component perpendicular to the z-axis. Thus, the emitted radiation will be linearly polarized with its electric vector oscillating in the plane defined by $\hat{\mathbf{z}}$ and the direction of the emitted radiation k (see Fig. 21.3). Further, the intensity of the radiation will vary as $\sin^2\theta$ $(= |\mathbf{e}\cdot\hat{\mathbf{z}}|^2)$.

For the

$$m_f = m_i + 1 \tag{58}$$

transition

$$P_z = 0 \quad \text{and} \quad P_y = -iP_x \tag{59}$$

(see Eqs. 50 and 51). Thus the electric field associated with the emitted radiation will have no component along the z-axis. Consequently, if k is along $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$, the emitted radiation is plane polarized along the $\hat{\mathbf{y}}$ and $\hat{\mathbf{x}}$ directions respectively and if k is along $\hat{\mathbf{z}}$, the radiation is left circularly polarized. For k in any other direction, the polarization is elliptical.

As an example, we consider the ${}^1D_2 \rightarrow {}^1P_1$ transition (as in the case of the Cd 6438.17 Å line). Since we have neglected spin, we consider only singlet states. If we place the atom in a magnetic field in the z-direction, the levels will split up as shown in Fig. 21.4 (this is the Zeeman effect). Using the selection rules, we have

$$\begin{array}{c}\text{viewed} \perp \text{to } \mathbf{B}\\ \text{[i.e., } \mathbf{k} \text{ along } \mathbf{x} \text{ (say)]}\end{array} \begin{cases} m_f = m_i \text{ (i.e., } \Delta m = 0\text{) transitions plane polarized } \parallel \text{ to } \mathbf{B} \text{ (}p\text{ components)} \\ m_f = m_i \pm 1 \text{ (i.e., } \Delta m = \pm 1\text{) transitions plane polarized } \perp \text{ to } \mathbf{B} \text{ (}s\text{ components)}\cdot \end{cases}$$

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*$\hat{\mathbf{e}}$ represents the polarization of the emitted radiation, even for spontaneous emissions. This is explicitly shown in the next chapter.

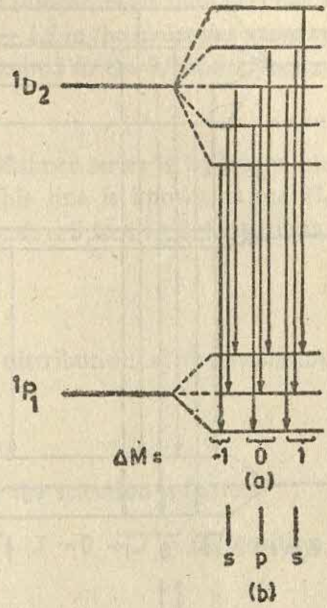

Fig. 21.4 (*a*) The Zeeman pattern for the $^1D_2 \rightarrow {}^1P_1$ transition. (*b*) If viewed ⊥ to **B**, three lines are seen; if light polarized ∥ to **B** is allowed to reach the film then only the *p* components are seen and if light polarized ⊥ to **B** is allowed to reach the film then only the *s* components are seen.

$$\begin{array}{l} \text{viewed} \parallel \text{to } \mathbf{B} \\ [\text{i.e., } \mathbf{k} \text{ along } \hat{\mathbf{z}}] \end{array} \left\{ \begin{array}{l} m_f = m_i \text{ (i.e., } \Delta m = 0) \text{ transitions not seen (} p \text{ components)} \\ m_f = m_i \pm 1 \text{ (i.e., } \Delta m = \pm 1) \text{ transitions circularly polarized (} s \text{ components).} \end{array} \right.$$

This is known as the normal Zeeman effect and the lines are known as the Lorentz triplet.

In the presence of spin-orbit interaetion of the form $\xi(r)\,\mathbf{L}\cdot\mathbf{s}$, the atomic states are characterized by the quantum numbers l, s, j and m_j (see Problem 18.2). The corresponding selection rules are

$$\left.\begin{array}{l} \Delta j \;\; = 0, \pm 1 \\ \Delta l \;\; = \pm 1 \\ \Delta m_j = 0, \pm 1 \\ \text{However,} \\ (m_j)_i = 0 \rightarrow (m_j)_f = 0 \text{ transition forbidden if } \Delta j = 0 \end{array}\right\} \quad (61)$$

It may be noted that the transition $\Delta j = 0$ is allowed but $j_i = j_f = 0$ transition is not allowed. The Zeeman pattern for the $^2P_{3/2,1/2} \rightarrow {}^2S_{1/2}$ transition (as in the case for *D* lines of Sodium) is shown in Fig. 21.5 (see also Problem 21.7).

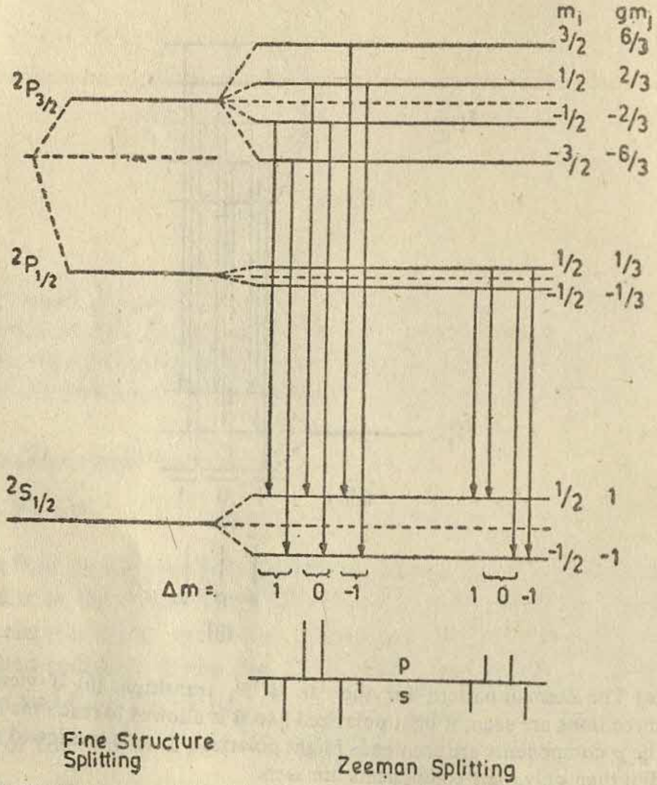

Fig. 21.5 The Zeeman pattern for the $^2P_{3/2,1/2} \to {}^2S_{1/2}$ doublet in sodium. Notice that the Zeeman splitting is different for different levels [the splitting is proportional to gm_j, see Eq. (66) of Chapter 18]. The lower part of the figure shows that in the transition there are two *p* components and four *s* components.

PROBLEMS

PROBLEM 21.1

Show that for optical frequencies, at thermal equilibrium (corresponding to $T \sim 1000°\text{K}$), the number of spontaneous emissions far exceeds the number of stimulated emissions.

PROBLEM 21.2

Derive Eqs. (50) and (51) and hence the selection rules.

PROBLEM 21.3

For the $2P \to 1S$ transition in hydrogen atom, prove that

$$|\langle S|\mathbf{r}|2P\rangle|^2 = \left|\int \psi_{1S}^* \,\mathbf{r}\, \psi_{2P}\, d\tau\right|^2 = 2^5\left(\frac{2}{3}\right)^{10} a_0^2$$

independent of the initial value of *m*. Using the above result calculate the corresponding lifetime for spontaneous emissions.

PROBLEM 21.4

Calculate the relative intensities of the two lines corresponding to the transitions $3P \rightarrow 1S$ and $2P \rightarrow 1S$ in the hydrogen atom spectrum assuming that equal number of atoms are excited to the $3P$ and $2P$ states.

PROBLEM 21.5

The first line of the Balmer series in hydrogen atom corresponds to the $n = 3$ to $n = 2$ transition, this line is known as the H_α line. What would be the selection rules for the $n = 3$ to $n = 2$ transitions and the corresponding lifetimes ?

PROBLEM 21.6

Obtain the angular distribution of the radiation emitted by the $nP \rightarrow n'S$ transition.

PROBLEM 21.7

For $L - S$ coupling the selection rules are

$$\begin{aligned}
\Delta J &= 0, \pm 1 \ (J = 0 \rightarrow J = 0 \text{ transition forbidden}) \\
\Delta L &= \pm 1 \\
\Delta S &= 0 \\
\Delta M &= 0, \pm 1 \ (M = 0 \rightarrow M = 0 \text{ transition forbidden for } \Delta J = 0)
\end{aligned} \tag{62}$$

Using the above selection rules, show that in the Zeeman splitting of the transitions given in the first column of Table 21.1 the number of p and s components would be as given in the second and third columns.

TABLE 21.1

Transition	*Number of p-components*	*Number of s-components*
${}^2D_{5/2} \rightarrow {}^2P_{3/2}$	4	8
${}^2G_{7/2} \rightarrow {}^2F_{5/2}$	6	12
${}^3P_2 \rightarrow {}^3S_1$	3	6
${}^3P_1 \rightarrow {}^3S_1$	2	4
${}^3P_0 \rightarrow {}^3S_1$	1	2

PROBLEM 21.8

Assuming that the atom can exist in two possible states characterized by the wavefunctions $\psi_1(\mathbf{r})$ and ψ $(\mathbf{r})$ and considering the atom-field interaction to be of the form given by Eq. (12), obtain a solution of the Schrödinger equation in the rotating wave approximation (i.e., neglect terms whose time dependences are of the form $\exp [\pm i(\omega + \omega_{21})t]$).

PROBLEM 21.9

Using Eqs. (100) and (101) of Chapter 9 for $\psi(n, l, \frac{1}{2}, j, m_j)$ derive the selection rules given by Eq. (61).

PROBLEM 21.10

In Sec. 21.3 we had considered interaction of an atom with a radiation field having continuous spectrum of frequency. Carry out as imilar analysis for a near monochromatic wave interacting with an atom having a broad frequency response.

SOLUTIONS

SOLUTION 21.1

At thermal equilibrium, the ratio of the number of spontaneous to stimulated emissions is given by

$$\frac{A}{Bu(\omega)} = \exp\left(\frac{\hbar\omega}{k_B T}\right) - 1$$

Now

$$\frac{k_B T}{\hbar} \simeq \frac{1.38 \times 10^{-23}\,(\text{J}/^\circ\text{K}) \times 10^{3}\,(^\circ\text{K})}{1.054 \times 10^{-34}\,(\text{J sec})} \cong 1.3 \times 10^{14}\ \text{sec}^{-1}$$

For the optical region $\lambda \sim 6000$ Å and hence $\omega \sim 3 \times 10^{15}\ \text{sec}^{-1}$. Thus $A/Bu(\omega) \gg 1$ and the transition is predominantly due to spontaneous transitions.

SOLUTION 21.2

The selection rule $\Delta m = 0, \pm 1$ can be derived easily from the fact that the φ-dependence of Y_{lm} is of the form $\exp(im\varphi)$ and that

$$z = r\cos\theta, \qquad x \pm iy = r \sin\theta\, e^{\pm i\varphi}$$

Since

$$\int_0^{2\pi} e^{i(m'-m)\varphi}\, d\varphi = 0 \quad \text{for} \quad m' \neq m$$

the φ integration in $\int \psi_f^* z\, \psi_i\, d\tau$ leads to the selection rule $m_f = m_i$ and the φ integration in $\int \psi_f^* (x \pm iy)\, \psi_i\, d\tau$ leads to $m_f = m_i \pm 1$.

In order to obtain Eqs. (50) and (51), we note that

$$\left.\begin{aligned} z = r\cos\theta \quad &= r\left(\frac{4\pi}{3}\right)^{1/2} Y_{10} \\ &\text{and} \\ x \pm iy = r\sin\theta\, e^{\pm i\varphi} &= \mp r\left(\frac{8\pi}{3}\right)^{1/2} Y_{1,\pm 1} \end{aligned}\right\} \qquad (63)$$

Further, if we use the following recurrence relations

$$\left(\frac{8\pi}{3}\right)^{1/2} Y_{1,1}Y_{l,m-1} = \left[\frac{(l+m)(l+1+m)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m} - \left[\frac{(l-m)(l+1-m)}{(2l+1)(2l-1)}\right]^{1/2} Y_{l-1,m} \tag{64}$$

$$\left(\frac{4\pi}{3}\right)^{1/2} Y_{1,0}Y_{l,m} = \left[\frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m} - \left[\frac{(l-m)(l+m)}{(2l+1)(2l-1)}\right]^{1/2} Y_{l-1,m} \tag{65}$$

$$\left(\frac{8\pi}{3}\right)^{1/2} Y_{1,-1}Y_{l,m+1} = \left[\frac{l-m)(l+1-m)}{(2l+1)\,(2l+3)}\right]^{1/2} Y_{l+1,m} - \left[\frac{(l+m)\,(l+1+m)}{(2l+1)\,(2l-1)}\right]^{1/2} Y_{l-1,m} \tag{66}$$

and also the orthonormality condition of spherical harmonics, we immediately get Eqs. (50) and (51) from which the selection rules (Eqs. 53 and 54) follow.

SOLUTION 21.3

We may directly use Eqs. (50) and (51); however, in this case, it is possible to calculate the matrix elements without using the recurrence relations (Eqs. 64 to 66). The eigenfunctions for the 2*P* and 1*S* states are

$$\psi_i = \psi_{2P} = R_{21}(r)\, Y_{1m}(\theta, \varphi) \tag{67}$$

and

$$\psi_f = \psi_{1S} = R_{10}(r)\, Y_{00}(\theta, \varphi) = \frac{1}{\sqrt{4\pi}}\, R_{10}(r) \tag{68}$$

Substituting for $R_{21}(r)$ and $R_{10}(r)$ (see Sec. 5.3) in Eq. (52) and carrying out the integration we get

$$G = 4\sqrt{6}\left(\frac{2}{3}\right)^5 a_0$$

Thus

$$z_{fi} = \int \psi_f^* z \psi_i \, d\tau = G \int \frac{1}{\sqrt{4\pi}} \sqrt{\frac{4\pi}{3}}\, Y_{10}\, Y_{1m}\, d\Omega = 4\sqrt{2}\left(\frac{2}{3}\right)^5 a_0\, \delta_{m,0} \tag{69}$$

Since

$$Y_{1,-m} = (-1)^m\, Y_{1,m}^*(\theta, \varphi)$$

we have

$$(x \pm iy)_{fi} = G \int \frac{1}{\sqrt{4\pi}} \left(\pm \sqrt{\frac{8\pi}{3}}\, Y^*_{1,\mp 1} \right) Y_{1,m}\, d\Omega$$
$$= \pm 8 \left(\frac{2}{3} \right)^5 a_0\, \delta_{m,\mp 1} \tag{70}$$

Thus

$$x_{fi} = 4(\tfrac{2}{3})^5\, a_0\, [\delta_{m,-1} - \delta_{m,1}] \tag{71}$$

and

$$y_{fi} = -\,4i\, (\tfrac{2}{3})^5\, a_0\, [\delta_{m,-1} + \delta_{m,1}] \tag{72}$$

It can be easily verified that

$$|\,\mathbf{r}_{fi}\,|^2 = |\,x_{fi}\,|^2 + |\,y_{fi}\,|^2 + |\,z_{fi}\,|^2 = 2^5\, (\tfrac{2}{3})^{10}\, a_0^2 \tag{73}$$

for $m = +1$, 0 and -1 which gives the result as given by Eq. (44). The lifetime calculation is given in Sec. 21.4.

SOLUTION 21.4

Since the intensity of the emitted line is proportional to the energy emitted per second, the required ratio is given by

$$R = \frac{\hbar\omega_1 A_1}{\hbar\omega_2 A_2} \tag{74}$$

where

$$\hbar\omega_1 = E_{2P} - E_{1S} = [-\tfrac{1}{4} + 1]\, E_H = \tfrac{3}{4}\, E_H$$
$$\hbar\omega_2 = E_{3P} - E_{1S} = [-\tfrac{1}{9} + 1]\, E_H = \tfrac{8}{9}\, E_H$$
$$A_1 = A\,(2P \to 1S) = \frac{4}{3}\, \alpha\, \frac{\omega_1^3}{c^2} \left| \int \psi^*_{1S}\, \mathbf{r} \psi_{2P}\, d\tau \right|^2$$

and

$$A_2 = A\,(3P \to 1S) = \frac{4}{3}\, \alpha\, \frac{\omega_2^3}{c^2} \left| \int \psi^*_{1S}\, \mathbf{r} \psi_{3P}\, d\tau \right|^2$$

Using the expressions for $R_{31}(r)$, $R_{21}(r)$ and $R_{20}(r)$ (given in Appendix J) in Eq. (52) and carrying out the integrations we get

$$G_1 = G(2P \to 1S) = 4\sqrt{6} \left(\frac{2}{3} \right)^5 a_0 = \frac{256}{81\sqrt{6}}\, a_0$$
$$G_2 = G(3P \to 1S) = \frac{1}{4\sqrt{6}} \left(\frac{3}{2} \right)^4 a_0 = \frac{81}{64\sqrt{6}}\, a_0$$

The angular integrals will be the same for both the transitions and the values will be the same as calculated in the previous solution. Thus

$$R = \left(\frac{\frac{3}{4} E_H}{\frac{8}{9} E_H} \right)^4 \left(\frac{256 \times 64}{81 \times 81} \right)^2 = \frac{256}{81} \simeq 3.16$$

SOLUTION 21.5

For the $n = 3$ to $n = 2$ transition one could have the following possible transitions : $3S \rightarrow 2P$, $3P \rightarrow 2S$, $3D \rightarrow 2P$. In order to determine the total transition probability for a given initial state, one must sum over the possible final states. Thus, for the $|3,0,0\rangle$ state, the final state could be either of the following three states : $|2, 1, 1\rangle$, $|2, 1, 0\rangle$ and $|2, 1, -1\rangle$ and the total transition probability (per unit time) would be given by

$$A(3S \rightarrow 2P) = \frac{4}{3} \alpha \frac{\omega^3}{c^2} \sum_{m=1,0,-1} \left| \langle 2, 1, m \,|\, \mathbf{r} \,|\, 3, 0, 0 \rangle \right|^2 \tag{75}$$

where

$$\omega = \frac{E_3 - E_2}{\hbar}$$

Thus using Eqs. (50) and (51)

$$\begin{aligned} A\,(3S \rightarrow 2P) = \frac{4}{3} \alpha \frac{\omega^3}{c^2} \Big[& |\langle 2, 1, 1 \,|\, x \,|\, 3, 0, 0 \rangle|^2 \\ & + |\langle 2, 1. 1 \,|\, y \,|\, 3, 0, 0 \rangle|^2 \\ & + |\langle 2, 1, 0 \,|\, z \,|\, 3, 0, 0 \rangle|^2 \\ & + |\langle 2, 1, -1 \,|\, x \,|\, 3, 0, 0 \rangle|^2 \\ & + |\langle 2, 1, -1 \,|\, y \,|\, 3, 0, 0 \rangle|^2 \Big] \end{aligned} \tag{76}$$

Each of the matrix elements could be calculated easily. For the $3P \rightarrow 2S$ transition one should consider a particular initial state, say $|3, 1, 0\rangle$ and calculate the transition probability, which would be

$$\begin{aligned} A(|3, 1, 0\rangle \rightarrow |2, 0, 0\rangle) &= \frac{4}{3} \alpha \frac{\omega^3}{c^2} |\langle 2, 0, 0 \,|\, \mathbf{r} \,|\, 3, 1, 0 \rangle|^2 \\ &= \frac{4}{3} \alpha \frac{\omega^3}{c^2} |\langle 2, 0, 0 \,|\, z \,|\, 3, 1, 0 \rangle|^2 \text{ [because } m_f = m_i, \text{ see Eqs. (50) and (51)]} \\ &= \frac{4}{9} \alpha \frac{\omega^3}{c^2} |G|^2 \end{aligned} \tag{77}$$

where we have used the relation

$$\iint Y_{00}^* \cos\theta \, Y_{10} \, d\Omega = \frac{1}{\sqrt{3}}$$

etc.

SOLUTION 21.6

Let the direction of propagation of the emitted radiation be denoted by $\mathbf{k}$ which makes the polar angles Θ, Φ with respect to the z-axis. Let $\hat{\mathbf{e}}_1$ represent an unit vector in the $\mathbf{k} - \hat{\mathbf{z}}$ plane and perpendicular to $\mathbf{k}$ and let $\hat{\mathbf{e}}_2$ be the unit vector normal to the $\mathbf{k} - \hat{\mathbf{z}}$ plane. Thus the Cartesion components of $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are

$$\begin{array}{llll} \lambda = 1, \hat{\mathbf{e}}_1: & -\cos\Theta\cos\Phi & -\cos\Theta\sin\Phi & \sin\Theta \\ \lambda = 2; \hat{\mathbf{e}}_2: & \sin\Phi & -\cos\Phi & \end{array}$$

The angular distribution of the emitted radiation is proportional to

$$\left| \int \psi_f^* \hat{\mathbf{e}}_\lambda \cdot \mathbf{r}\psi_i \, d\tau \right|^2 \sin\Theta \, d\Theta \, d\Phi$$

Let us first consider $\lambda = 1$ for which

$$\begin{aligned} \hat{\mathbf{e}}_\lambda \cdot \mathbf{r} &= r\,[e_{\lambda x} \sin\theta\cos\varphi + e_{\lambda y} \sin\theta\sin\varphi + e_{\lambda z}\cos\theta] \\ &= r\left[\left(\frac{8\pi}{3}\right)^{1/2} \frac{1}{2}(-Y_{1,1} + Y_{1,-1})(-\cos\Theta\cos\Phi)\right. \\ &\quad + \left(\frac{8\pi}{3}\right)^{1/2} \frac{1}{2i}(-Y_{1,1} - Y_{1,-1})(-\cos\Theta\sin\Phi) \\ &\quad \left. + \left(\frac{4\pi}{3}\right)^{1/2} Y_{1,0}\sin\Theta \right] \end{aligned}$$

Thus for the $nP \to n'S$ transition

$$\begin{aligned} \int \psi_f^* \hat{\mathbf{e}}_1 \cdot \mathbf{r}\psi_i \, d\tau = G \iint Y_{00} \left(\frac{2\pi}{3}\right)^{1/2} [(Y_{1,1} - Y_{1,-1})\cos\Theta\cos\Phi \\ - i(Y_{1,1} + Y_{1,-1})\cos\Theta\sin\Phi \\ + \sqrt{2}\, Y_{10}\sin\Theta]\, Y_{1,m} \sin\theta d\theta\, d\varphi \end{aligned}$$

where G is given by Eq. (52). Simple integrations give

$$\int \psi_f^* \hat{\mathbf{e}}_1 \cdot \mathbf{r}\psi_i \, d\tau = \begin{cases} \dfrac{G}{\sqrt{6}} \cos\Theta\, e^{i\Phi} & \text{for } m = 1 \\ \dfrac{G}{\sqrt{3}} \sin\Theta & \text{for } m = 0 \\ -\dfrac{G}{\sqrt{6}} \cos\Theta\, e^{-i\Phi} & \text{for } m = -1 \end{cases} \tag{78}$$

Similarly for $\lambda = 2$

$$\int \psi_f^* \hat{\mathbf{e}}_2 \cdot \mathbf{r}\psi_i \, d\tau = \begin{cases} \dfrac{i}{\sqrt{6}} e^{i\Phi} & \text{for } m = 1 \\ 0 & \text{for } m = 0 \\ \dfrac{i}{\sqrt{6}} e^{-i\Phi} & \text{for } m = -1 \end{cases} \tag{79}$$

If we write the intensity distribution as

$$I_\lambda d\Omega = I_0 f_\lambda(\Theta, \Phi) \sin \Theta d\Theta d\Phi \tag{80}$$

the values of f_λ are given in the table

m	$\lambda = 1$	$\lambda = 2$
1	$\frac{1}{2}\cos^2 \Theta$	$\frac{1}{2}$
0	$\sin^2 \Theta$	0
-1	$\frac{1}{2}\cos^2 \Theta$	$\frac{1}{2}$

Notice that $\lambda = 2$ case is isotropic.

SOLUTION 21.8

Assuming that the atom can exist in only two possible states described by the wavefunctions $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ we get from Eq. (18)

$$i\hbar \frac{dC_1}{dt} = \tfrac{1}{2} \mathcal{E}_0 \mathcal{D}_{12} C_2(t) \left[e^{-i(\omega'-\omega)t} + e^{-i(\omega'+\omega)t}\right] \tag{81}$$

and

$$i\hbar \frac{dC_2}{dt} = \tfrac{1}{2} \mathcal{E}_0 \mathcal{D}_{21} C_1(t) \left[e^{i(\omega'+\omega)t} + e^{i(\omega'-\omega)t}\right] \tag{82}$$

where

$$\omega' = (E_2 - E_1)/\hbar = \omega_{21} = -\omega_{12}$$

and use has been made of the fact that

$$\int \psi_1^* \mathbf{r} \psi_1 d\tau = \int \psi_2^* \mathbf{r} \psi_2 d\tau = 0 \tag{83}$$

and therefore $\mathcal{D}_{11} = \mathcal{D}_{22} = 0$. In the rotating wave approximation*, we neglect the terms $\exp [\pm i(\omega' + \omega)t]$ because of their very rapid oscillations to obtain

$$\frac{dC_1}{dt} = -\frac{i}{2\hbar} \mathcal{E}_0 \mathcal{D}_{12} C_2(t) e^{i(\omega-\omega')t} \tag{84}$$

and

$$\frac{dC_2}{dt} = -\frac{i}{2\hbar} \mathcal{E}_0 \mathcal{D}_{21} C_1(t) e^{-i(\omega-\omega')t} \tag{85}$$

---

*Salzman (1971) has obtained exact numerical solution of the Schrödinger equation without using the rotating wave approximation. The final result for $| C_2(t) |^2$ is the same except for the presence of a weak high frequency oscillation superimposed on the solution (see Fig. 21.6).

We assume a solution of the type

$$C_1(t) = e^{i\Omega t} \tag{86}$$

then from Eq. (84)

$$C_2(t) = -\frac{2\hbar\Omega}{\mathcal{E}_0\mathcal{D}_{12}} e^{i(\Omega-\omega+\omega')t} \tag{87}$$

Substituting (86) and (87) in (85) we get

$$\Omega^2 + (\omega' - \omega)\Omega - \tfrac{1}{4}\Omega_0^2 = 0 \tag{88}$$

where

$$\Omega_0^2 = \frac{\mathcal{D}_{12}\mathcal{D}_{21}\mathcal{E}_0^2}{\hbar^2} = \frac{\mathcal{D}^2\mathcal{E}_0^2}{\hbar^2} \tag{89}$$

and

$$\mathcal{D} = \mathcal{D}_{12} = \mathcal{D}_{21} \tag{90}$$

Equation (88) gives

$$\Omega_{1,2} = \tfrac{1}{2}[-(\omega' - \omega) \pm \{(\omega' - \omega)^2 + \Omega_0^2\}] \tag{91}$$

Thus the general solutions of Eqs. (84) and (85) will be

$$C_1(t) = A_1\, e^{i\Omega_1 t} + A_2\, e^{i\Omega_2 t} \tag{92}$$

and

$$C_2(t) = -\frac{2}{\Omega_0}\, e^{i(\omega'-\omega)t}\, [A_1\Omega_1\, e^{i\Omega_1 t} + A_2\Omega_2\, e^{i\Omega_2 t}] \tag{93}$$

A_1 and A_2 can be determined from initial conditions. For example, if the atom is in the ground state, then

$$C_1(0) = 1,\ C_2(0) = 0 \tag{94}$$

Which gives

$$|C_2(t)|^2 = \left[\frac{\sin(\Omega' t/2)}{\Omega'/2}\right]^2 \left(\frac{\Omega_0}{2}\right)^2 \tag{95}$$

where

$$\Omega' = [(\omega' - \omega)^2 + \Omega_0^2]^{1/2} \tag{96}$$

Equation (95) gives the transition probability for absorption which has been shown in Fig. 21.6. Also shown in the figure are the results of the exact numerical calculations without resorting to the rotating wave approximation.

Now, at resonance, $\omega = \omega'$ and

$$|C_2(t)|^2 = \sin^2 \Omega_0 t/2 \tag{97}$$

which shows that the system flip-flops between states 1 and 2.

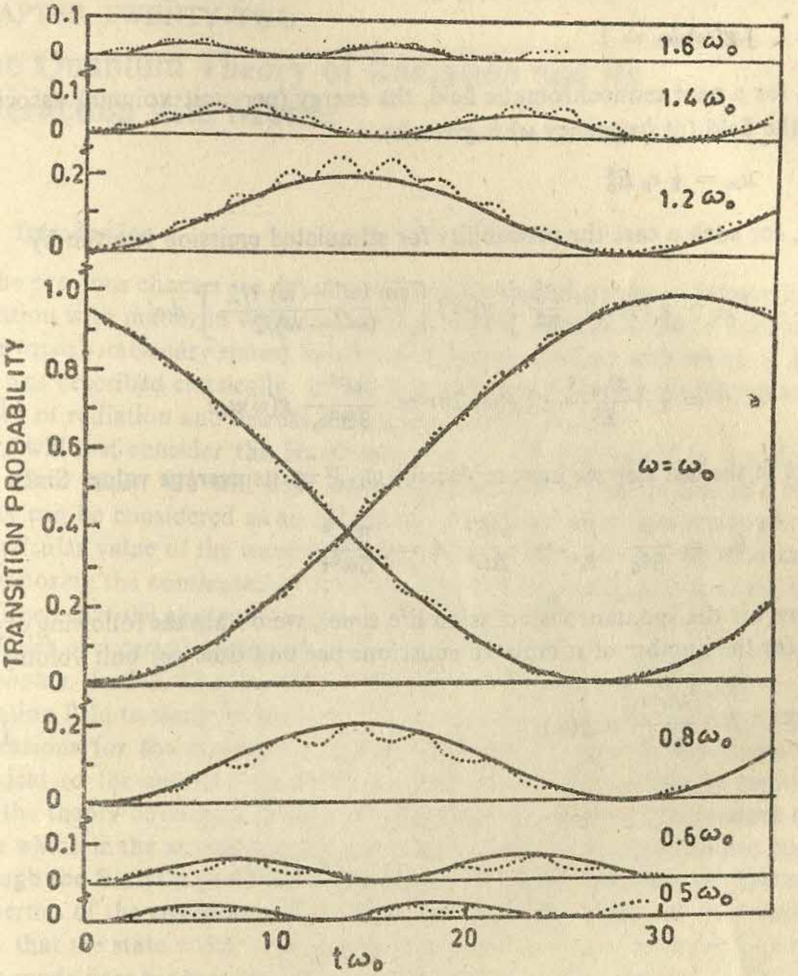

Fig. 21.6 Variation of the transition probability for a two level system for different frequencies of the electromagnetic field ω as a function of time. The curves correspond to $\mathscr{D}\mathcal{E}_0/\hbar = 0.1\omega'$. The solid line corresponds to Eq. (95) and the dotted curve corresponds to an exact numerical computation. Notice the presence of a weak high frequency oscillation present in the exact calculation which is due to the presence of the $\exp[\pm i(\omega + \omega')t]$ terms in Eqs. (81) and (82). The curve for $\omega = \omega_0$ has been cut at $t\omega_0 = 36$ and shifted to the origin. (After Salzman; 1971).

It may be pointed out that the solutions obtained here are exact when $\omega = 0$ provided $\mathscr{D}_{12}$ is replaced by $2\mathscr{D}_{12}$.

SOLUTION 21.10

We consider a nearly monochromatic field (which is indeed true for a laser) interacting with atoms characterized by the line shape function $g(\omega)$. Thus $N_1 g(\omega)d\omega$ and $N_2 g(\omega)d\omega$ represent the number of atoms per unit volume in levels 1 and 2 respectively which are capable of interacting with radiation of frequency between ω and $\omega + d\omega$. Obviously*,

$$\int g(\omega) d\omega = 1 \tag{98}$$

Now, for a near monochromatic field, the energy (per unit volume) associated with the field (at frequency ω) is given by

$$u_\omega = \tfrac{1}{2} \epsilon_0 E_0^2 \tag{99}$$

Thus, for such a case the probability for stimulated emission is given by

$$\begin{aligned} \Gamma_{21} &= \tfrac{1}{4} \mid \mathscr{D}_{12} \mid^2 \frac{\mathscr{E}_0^2}{\hbar^2} \int g(\omega') \left[\frac{\sin (\omega' - \omega)\, t/2}{(\omega' - \omega)/2} \right]^2 d\omega' \\ &\simeq \tfrac{1}{4} \frac{\mid \mathscr{D}_{12} \mid^2}{\hbar^2} \mathscr{E}_0^2\, g(\omega)\, 2\pi t \simeq \frac{\pi P^2}{3\hbar^2 \epsilon_0} g(\omega) u_\omega t \end{aligned} \tag{100}$$

where in the last step we have replaced $\mid \mathscr{D}_{12} \mid^2$ by its average value. Since

$$B_{2_1} = \frac{\pi}{3\epsilon_0} \frac{P^2}{\hbar^2} = \frac{\pi^2 C^3}{\hbar \omega^3} A = \frac{\pi^2 C^3}{\hbar \omega^2 \tau} \tag{101}$$

(where τ is the spontaneous emission life time), we obtain the following expression for the number of stimulated emissions per unit time per unit volume

$$N_1 \frac{\pi^2 C^3}{\hbar \omega^2 \tau} u_\omega g(\omega) \tag{102}$$

---

*Different types of line shape functions have been discussed by Thyagarajan ana Ghatak (1981)—see also Problem 22.3.

CHAPTER TWENTY-TWO

The Quantum Theory of Radiation and its Interaction with Matter

22.1 Introduction

In the previous chapter we developed the semiclassical theory of interaction of radiation with matter in which matter, i.e., atoms, were assumed to exist in discrete (quasi-stationary states) but the electromagnetic field with which it interacts was described classically. In this chapter we will develop the fully quantum theory of radiation and discuss its interaction with matter.

We will first consider the Hamiltonian of an atomic system in a radiation field (Sec. 22.2). We will next show that the electromagnetic field in a closed cavity can be considered as an infinite set of oscillators, each corresponding to a particular value of the wave-vector and a particular direction of polarization. By imposing the commutation relations between the canonical variables, it will be shown that the energy of each oscillator can increase or decrease by integral multiples of a certain quantum of energy; this quantum of energy is known as the *photon*. In Sec. 22.4 we will use the quantum mechanical description of the radiation field to study its interaction with an atom and thereby obtain explicit expressions for the Einstein A and B coefficients which will be shown to be identical to the results obtained in the previous chapter. It may be mentioned that the theory developed in Sec. 22.4 automatically leads to spontaneous emissions which in the semiclassical theory had to be introduced in an *ad hoc* manner through the Einstein coefficients (see Sec. 21.4). In Sec. 22.5 we will discuss the properties of the eigenstates of the Hamiltonian of the radiation field and will show that the state which corresponds to a given number of photons for a particular mode does *not* correspond to the classical plane wave. Indeed, in Sec. 22.6, we will show that the eigenstates of the annihilation operator (which are known as the coherent states) resemble the classical plane wave for large intensities. In fact when a laser is operated much beyond the threshold, it generates a coherent state excitation of a cavity mode. Finally, in Sec. 22.7, we will show that it is difficult to give a quantum mechanical description of the phase of the electromagnetic wave.

22.2 The Hamiltonian

The Hamiltonian of an atomic system in a radiation field can be written as

$$\begin{aligned} H &= H_0 + H' \\ &= H_a + H_r + H' \end{aligned} \tag{1}$$

where H_a represents the Hamiltonian of the atom, H_r the Hamiltonian corresponding to the pure radiation field, which is given by*

$$H_r = \tfrac{1}{2} \int (\epsilon_0 \mathcal{E} \cdot \mathcal{E} + \mu_0 \mathcal{H} \cdot \mathcal{H})\, d\tau \qquad (2)$$

and H' represents the interaction between the atom and the radiation field. For example, for a non-relativistic electron (of charge $-q$) in a radiation field, we have

$$H = \frac{1}{2m} (\mathbf{p} + q\mathbf{A})^2 + V + H_r \qquad (3)$$

since the recipe is to replace the electron momentum operator $\mathbf{p}$ by $\mathbf{p} + q\mathbf{A}$ (see Sec. 18.2), where $\mathbf{A}$ is the vector potential and V is the potential energy of the electron. We can rewrite Eq. (3) as

$$H = H_0 + H'$$

where

$$H_0 = H_a + H_r$$

$$H_a = \frac{p^2}{2m} + V(r) \qquad (4)$$

$$H' = + \frac{q}{2m}\left(\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A} \right) \frac{q^2}{2m} A^2 \qquad (5)$$

and H_r is given by Eq. (2). In Sec. 22.4 we will treat H' as a perturbation and study the transitions between eigenstates of H_0. The term $(q^2/2m)A^2$ appearing in the expression for H' usually represents a very small perturbation and hence will be neglected. Thus the interaction term is given by

$$H' = + \frac{q}{m} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) \qquad (6)$$

Now

$$\begin{aligned} \mathbf{p} \cdot \mathbf{A}\Psi &= -i\hbar \nabla \cdot (\mathbf{A}\Psi) \\ &= -i\hbar[(\nabla \cdot \mathbf{A})\Psi + \mathbf{A} \cdot \nabla\Psi] \\ &= \mathbf{A} \cdot \mathbf{p}\Psi \end{aligned}$$

where we have chosen the Coulomb gauge in which $\nabla \cdot \mathbf{A} = 0$ (see Sec. 18.3). Thus

$$H' = \frac{q}{m}\, \mathbf{A} \cdot \mathbf{p} = \frac{q}{m}\, \mathbf{p} \cdot \mathbf{A} \qquad (7)$$

There are now two ways of proceeding further. The first is to treat the electromagnetic field classically; this has indeed been done in the previous chapter.

---

*In Eq. (2) ϵ_0 and μ_0 represent the dielectric permittivity and magnetic permeability of free space, $\mathcal{E}$ and $\mathcal{H}$ represent the electric and magnetic fields associated with the radiation field.

The second and more powerful method is to quantize the radiation field and calculate rates of transition between states of matter and quanta; this will be done in Secs. 22.3 and 22.4. However, before we do so, we will first show (in Sec. 22.2.1) that the interaction term given by Eq. 12 of the previous chapter is consistent with Eq. (7) under certain approximation which is known as the *dipole approximation.*

22.2.1 THE INTERACTION TERM IN THE SEMICLASSICAL THEORY OF RADIATION

For a plane electromagnetic wave, the vector potential can be written in the form

$$\mathbf{A} = \hat{\mathbf{e}} A_0 \cos(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{8}$$

where $\hat{\mathbf{e}}$ represents the unit vector along $\mathbf{A}$ (denoting the polarization of the wave), and

$$\mathbf{k} = \frac{\omega}{c}\,\hat{\mathbf{k}} \tag{9}$$

where $\hat{\mathbf{k}}$ represents the unit vector along the direction of propagation. The condition $\nabla\cdot\mathbf{A} = 0$ gives

$$\hat{\mathbf{e}}\cdot\mathbf{k} = 0 \tag{10}$$

implying that $\hat{\mathbf{e}}$ is at right angles to the direction of propagation, i.e., the wave is transverse. The electric field is given by

$$\mathcal{E} = -\frac{\partial \mathbf{A}}{\partial t} = -\hat{\mathbf{e}}\mathcal{E}_0 \sin(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{11}$$

where

$$\mathcal{E}_0 = \omega A_0 \tag{12}$$

Now

$$\begin{aligned} H' &= \frac{q}{m}\,\mathbf{A}\cdot\mathbf{p} \\ &= \frac{q\mathcal{E}_0}{2m\omega}\,\hat{\mathbf{e}}\{\exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)] + \exp[-i(\mathbf{k}\cdot\mathbf{r} - \omega t)]\}\cdot\mathbf{p} \end{aligned}$$

The matrix element of transition is given by (cf. Eq. 17 of Chapter 21)

$$\begin{aligned} H'_{sn} = \langle s \mid H' \mid n\rangle = \frac{q\mathcal{E}}{2m\omega}\,\hat{\mathbf{e}}\cdot[\langle s \mid e^{i\mathbf{k}\cdot\mathbf{r}}\,\mathbf{p} \mid n\rangle\, e^{-i\omega t} \\ + \langle s \mid e^{-i\mathbf{k}\cdot\mathbf{r}}\,\mathbf{p} \mid n\rangle e^{i\omega t}] \end{aligned} \tag{13}$$

where the kets $\mid n\rangle$ and $\mid s\rangle$ are eigenstates of the atomic Hamiltonian H_0

and represent the initial and final states. Now

$$e^{\pm i\mathbf{k}\cdot\mathbf{r}} = 1 \pm i\mathbf{k}\cdot\mathbf{r} - \frac{1}{2!}(\mathbf{k}\cdot\mathbf{r})^2 + \ldots$$

Since atomic dimensions are $\sim 10^{-8}$ cm and for optical wavelength

$$k\left(=\frac{2\pi}{\lambda}\right) \sim 10^5\ \text{cm}^{-1}$$

we obtain (in the region of integration) $kr \ll 1$. Thus, negligible error will be involved if the exponential is replaced by unity* and the transition is said to be an electric dipole transition—a very important case. In this approximation

$$\langle s \mid e^{\pm i\mathbf{k}\cdot\mathbf{r}}\mathbf{p} \mid n\rangle \simeq \langle s \mid \mathbf{p} \mid n\rangle \tag{14}$$

Now the kets $\mid n\rangle$ and $\mid s\rangle$ are eigenkets** of the atomic Hamiltonian H_a

$$H_a \mid n\rangle = E_n \mid n\rangle = \hbar\omega_n \mid n\rangle \tag{15}$$

$$H_a \mid s\rangle = E_s \mid s\rangle = \hbar\omega_s \mid s\rangle \tag{16}$$

Further

$$H_a = \frac{p^2}{2m} + V(\mathbf{r})$$

Thus

$$\begin{aligned}[x, H_a] &= \left[x, \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V(\mathbf{r})\right] \\ &= \frac{1}{2m}([x, p_x]\,p_x + p_x[x, p_x]) \\ &= \frac{i\hbar}{m}\,p_x \end{aligned} \tag{17}$$

or,

$$\mathbf{p} = \frac{m}{i\hbar}[\mathbf{r}, H_a] \tag{18}$$

Hence

$$\begin{aligned}\langle s \mid \mathbf{p} \mid n\rangle &= \frac{m}{i\hbar}\langle s \mid \mathbf{r}H_a - H_a\mathbf{r} \mid n\rangle \\ &= \frac{m}{i\hbar}(E_n - E_s)\langle s \mid \mathbf{r} \mid n\rangle \\ &= \frac{m\omega_{ns}}{i}\langle s \mid \mathbf{r} \mid n\rangle \end{aligned} \tag{19}$$

---

*However, if the replacement of $e^{\pm i\mathbf{k}\cdot\mathbf{r}}$ by unity leads to a vanishing matrix element, one must use higher order terms like $(\pm i\,\mathbf{k}\cdot\mathbf{r})$, etc.; these are said to correspond to higher order transitions (see Problem 22.1)

**We may warn the reader of some confusion of notation. The initial and final states of the atomic Hamiltonian are also sometimes denoted by $\mid i\rangle$ and $\mid f\rangle$ and sometimes by $\mid a\rangle$ and $\mid b\rangle$.

where we have used Eq. (15) and conjugate of Eq. (16) and

$$\hbar\omega_{ns} = E_n - E_s$$

On substitution in Eq. (13), we get

$$\langle s \mid H' \mid n\rangle = \frac{q\mathcal{E}_0\omega_{ns}}{2\omega}\,\hat{\mathbf{e}}\cdot\langle s \mid \mathbf{r} \mid n\rangle\,[e^{i\omega t} - e^{-i\omega t}] \tag{20}$$

The above equation is of a form similar (although not identical) to that of Eq. (17) of the previous chapter. However, for $\omega \approx |\,\omega_{ns}\,|$ after one carries out the integration which leads to Eq. (22) of the previous chapter, one obtains identical expressions for probabilities of absorption and of emission (see Eq. 24 of the previous chapter).

22.3 Quantization of the Radiation Field

We now develop the second method mentioned in Sec. 22.1. In this method, the electromagnetic field is described in terms of numbers of photons in various states.

We consider first a pure radiation field. In Coulomb gauge, such a field can be derived from the vector potential A only, with $\Phi = 0$ and

$$\nabla\cdot\mathbf{A} = 0 \tag{21}$$

In this gauge, the magnetic and electric fields are given by (see Sec. 18.2)

$$\mathcal{B} = \mu_0\,\mathcal{H} = \nabla\times\mathbf{A} \tag{22}$$

and

$$\mathcal{E} = -\frac{\partial\mathbf{A}}{\partial t} \tag{23}$$

where we have assumed $\phi = 0$, since we are considering free space. Substituting for $\mathcal{H}$ and $\mathcal{E}$ in the Maxwell equation

$$\nabla\times\mathcal{H} = \frac{\partial\mathcal{D}}{\partial t} = \epsilon_0\,\frac{\partial\mathcal{E}}{\partial t} \tag{24}$$

we get

$$\nabla\times(\nabla\times\mathbf{A}) = -\,\epsilon_0\mu_0\,\frac{\partial^2\mathbf{A}}{\partial t^2} \tag{25}$$

If we now use the identity*

$$\nabla\times(\nabla\times\mathbf{A}) \equiv \nabla(\nabla\cdot\mathbf{A}) - \nabla^2\mathbf{A} = -\,\nabla^2\mathbf{A} \tag{26}$$

---

*It may be worthwhile to point out that the operator ∇^2 is *defined* by the following equation

$$\nabla^2\mathbf{A} \equiv \nabla(\nabla\cdot\mathbf{A}) - \nabla\times(\nabla\times\mathbf{A})$$

However,

$$(\nabla^2\mathbf{A})_x = \nabla\cdot(\nabla A_x)$$

i.e., a Cartesian component of $\nabla^2\mathbf{A}$ is div grad of the Cartesian component but

$$(\nabla^2\mathbf{A})_r \neq \nabla\cdot(\nabla A_r)$$

(because $\nabla \cdot \mathbf{A} = 0$), we finally obtain

$$\nabla^2 \mathbf{A} = \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} \tag{27}$$

where

$$c = (\epsilon_0 \mu_0)^{-1/2} \tag{28}$$

represents the speed of light in free space. Equation (27) represents the 3-dimensional wave equation. In order to solve the wave equation, we use the method of separation of variables

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r})\, q(t) \tag{29}$$

Thus

$$q(t)\, \nabla^2 \mathbf{A}(\mathbf{r}) = \mathbf{A}(\mathbf{r}) \frac{1}{c^2} \frac{d^2 q}{dt^2} \tag{30}$$

We next consider a Cartesian component (say the x-component) of $\mathbf{A}(\mathbf{r})$ which we denote by $A_x(\mathbf{r})$; thus

$$\frac{c^2}{A_x(\mathbf{r})} \nabla^2 A_x(\mathbf{r}) = \frac{1}{q(t)} \frac{d^2 q}{dt^2} = -\omega^2 \text{ (say)} \tag{31}$$

Thus

$$q(t) \sim e^{-i\omega t} \tag{32}$$

and

$$\nabla^2 A_x(\mathbf{r}) + k^2 A_x(\mathbf{r}) = 0 \tag{33}$$

where $k^2 = \omega^2/c^2$. The solutions of Eq. (33) are plane waves; and similarly if we consider the y and z components we obtain

$$\mathbf{A}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\, \hat{\mathbf{e}} \tag{34}$$

where $\mathbf{k} \cdot \mathbf{k} = k^2$, $\hat{\mathbf{e}}$ is the unit vector along $\mathbf{A}$. The condition $\nabla \cdot \mathbf{A} = 0$ gives us $\mathbf{k} \cdot \hat{\mathbf{e}} = 0$, implying the transverse character of the wave [see Eq. (10)].

The allowed values of $\mathbf{k}$ (and hence of ω) are determined from the boundary conditions. If we assume the radiation to be confined in a cubical cavity of volume $V\,(=L^3)$ and use the periodic boundary condition then

$$\mathbf{A}(x = 0, y, z) = \mathbf{A}(x = L, y, z) \text{ etc.} \tag{35}$$

giving

$$e^{ik_x L} = 1 = e^{ik_y L} = e^{ik_z L} \tag{36}$$

Thus

$$\left.\begin{aligned} k_x &= \frac{2\pi\, \nu_x}{L} \\ k_y &= \frac{2\pi\, \nu_y}{L} \\ k_z &= \frac{2\pi\, \nu_z}{L} \end{aligned}\right\} \nu_x, \nu_y, \nu_z = 0, \pm 1, \pm 2, \ldots \tag{37}$$

The complete solution of Eq. (27) is therefore given by

$$\mathbf{A}(\mathbf{r}, t) = \sum_{\lambda} [q_{\lambda}(t)\, \mathbf{A}_{\lambda}(\mathbf{r}) + q_{\lambda}^{*}(t)\, \mathbf{A}_{\lambda}^{*}(\mathbf{r})] \tag{38}$$

where

$$\mathbf{A}_{\lambda}(\mathbf{r}) = e^{i\mathbf{k}_{\lambda}\cdot\mathbf{r}}\, \hat{\mathbf{e}}_{\lambda} \tag{39}$$

$$q_{\lambda}(t) = |\, q_{\lambda}\, |\, e^{-i\omega_{\lambda} t} \tag{40}$$

and the subscript λ signifies the various modes of the field (see Eq. 37) including the two states of polarization. Thus, a particular value of λ corresponds to a particular set of values of ν_x, ν_y, ν_z and a particular direction of $\hat{\mathbf{e}}$. In Eq. (38) the second term on the RHS is complex conjugate of the first term making **A** necessarily real. Because of the allowed values of $\mathbf{k}_{\lambda}$ (see Eq. 37), we readily obtain

$$\iiint_V \mathbf{A}_{\lambda} \cdot \mathbf{A}_{\mu}^{*}\, d\tau = \iiint_V \mathbf{A}_{\lambda} \cdot \mathbf{A}_{-\mu}\, d\tau = V\, \delta_{\lambda,\mu} \tag{41}$$

where the integration is over the entire volume of the cavity. Using Eq. (38), we obtain the following expressions for the electric and magnetic fields:

$$\mathcal{E} = -\frac{\partial \mathbf{A}}{\partial t} = \sum_{\lambda} \mathcal{E}_{\lambda} \tag{42}$$

$$\mathcal{H} = \frac{1}{\mu_0}\, \nabla \times \mathbf{A} = \sum_{\lambda} \mathcal{H}_{\lambda} \tag{43}$$

where

$$\mathcal{E}_{\lambda} = i\omega_{\lambda}\, [q_{\lambda}(t)\, \mathbf{A}_{\lambda}(\mathbf{r}) - q_{\lambda}^{*}(t)\, \mathbf{A}_{\lambda}^{*}(\mathbf{r})] \tag{44}$$

and

$$\mathcal{H}_{\lambda} = \frac{i}{\mu_0}\, \mathbf{k}_{\lambda} \times [q_{\lambda}\mathbf{A}_{\lambda} - q_{\lambda}^{*}\mathbf{A}_{\lambda}^{*}] \tag{45}$$

The total energy of the radiation field is given by

$$H_r = \tfrac{1}{2} \int (\epsilon_0\, \mathcal{E} \cdot \mathcal{E} + \mu_0\, \mathcal{H} \cdot \mathcal{H})\, d\tau \tag{46}$$

Now

$$\frac{1}{2}\epsilon_0 \int_V \mathcal{E}\cdot\mathcal{E}\,d\tau = -\frac{1}{2}\epsilon_0 \int_V \sum_\lambda\sum_\mu \omega_\lambda\,\omega_\mu \Big[q_\lambda\, q_\mu \int \mathbf{A}_\lambda\cdot\mathbf{A}_\mu\,d\tau$$

$$- q_\lambda\, q_\mu^* \int \mathbf{A}_\lambda\cdot\mathbf{A}_\mu^*\,d\tau - q_\lambda^*\, q_\mu \int \mathbf{A}_\lambda^*\cdot\mathbf{A}_\mu\,d\tau$$

$$+ q_\lambda^*\, q_\mu^* \int \mathbf{A}_\lambda^*\cdot\mathbf{A}_\mu^*\,d\tau\Big]$$

$$= -\frac{1}{2}\epsilon_0 V \sum_\lambda\sum_\mu \omega_\lambda\,\omega_\mu\,[q_\lambda\, q_\mu\;{}_{\lambda,-\mu}$$

$$- q_\lambda q_\mu^*\;\delta_{\lambda,\mu} - q_\lambda^*\, q_\mu\,\delta_{\lambda,\mu} + q_\lambda^*\, q_\mu^*\,\delta_{\lambda,-\mu}]$$

$$= -\frac{1}{2}\epsilon_0 V \sum_\lambda \omega_\lambda^2\,[q_\lambda\, q_{-\lambda} + q_\lambda^*\, q_{-\lambda}^* - 2q_\lambda\, q_\lambda^*] \tag{47}$$

Similarly one can evaluate $\int \mathcal{H}\cdot\mathcal{H}\,d\tau$. The final result is

$$\frac{1}{2}\mu_0 \int \mathcal{H}\cdot\mathcal{H}\,d\tau = \frac{1}{2}\epsilon_0 V \sum_\lambda \omega_\lambda^2\,[q_\lambda\, q_{-\lambda} + q_\lambda^*\, q_{-\lambda}^* + 2\,q_\lambda\, q_\lambda^*] \tag{48}$$

where use has to be made of the vector identity

$$(\mathbf{a}\times\mathbf{b})\cdot(\mathbf{c}\times\mathbf{d}) = (\mathbf{a}\cdot\mathbf{c})\,(\mathbf{b}\cdot\mathbf{d}) - (\mathbf{b}\cdot\mathbf{c})\,(\mathbf{a}\cdot\mathbf{d}) \tag{49}$$

and the relation

$$k_\lambda^2 = \frac{\omega_\lambda^2}{c^2} = \epsilon_0\mu_0\,\omega_\lambda^2 \tag{50}$$

Thus

$$H_r = 2\epsilon_0\, V \sum_\lambda \omega_\lambda^2\, q_\lambda(t)\, q_\lambda^*(t) \tag{51}$$

We next introduce the dimensionless variables Q_λ and P_λ defined through the equations

$$Q_\lambda(t) = (\epsilon_0\, V)^{1/2}\,[q_\lambda(t) + q_\lambda^*(t)] \tag{52}$$

and

$$P_\lambda(t) = \frac{1}{i}\,(\epsilon_0\, V\,\omega_\lambda^2)^{1/2}\,[q_\lambda(t) - q_\lambda^*(t)] \tag{53}$$

Thus

$$q_\lambda(t) = (4\,\epsilon_0\, V\,\omega_\lambda^2)^{-1/2}\,[\omega_\lambda\, Q_\lambda(t) + iP_\lambda(t)] \tag{54}$$

$$q_\lambda^*(t) = (4\,\epsilon_0\, V\,\omega_\lambda^2)^{-1/2}\,[\omega_\lambda\, Q_\lambda(t) - iP_\lambda(t)] \tag{55}$$

and

$$H_r = \sum_{\lambda} H_{\lambda} \tag{56}$$

where[*]

$$H_{\lambda} = \frac{1}{2}\,(P_{\lambda}^2 + \omega_{\lambda}^2\, Q_{\lambda}^2) \tag{57}$$

The Hamiltonian given by Eq. (57) is identical to that of the linear harmonic oscillator (see Eq. 48 of Chapter 8 with $m = 1$) which suggests that the electromagnetic field can be regarded as an infinite set of harmonic oscillators, one corresponding to each value of $\mathbf{k}_{\lambda}$ and to a particular direction of polarization.

In order to quantize the electromagnetic field we use the same approach as in Sec. 8.9. We consider Q_{λ} and P_{λ} to be real operators satisfying the commutation relations (see Sec. 2.3)

$$[Q_{\lambda}(t), P_{\lambda}(t)] \equiv Q_{\lambda}(t)\, P_{\lambda}(t) - P_{\lambda}(t)\, Q_{\lambda}(t) = i\hbar \tag{58}$$

$$[Q(t), P_{\lambda}'(t)] = 0 \tag{59}$$

$$[Q_{\lambda}(t), Q_{\mu}(t)] = 0 = [P_{\lambda}(t), P_{\mu}(t)] \tag{60}$$

where all the operators are in the Heisenberg representation (see Sec. 8.12). We next introduce the dimensionless variables

$$a_{\lambda}(t) = \frac{1}{\sqrt{2\hbar\,\omega_{\lambda}}}\,[\omega_{\lambda}\, Q_{\lambda}(t) + iP_{\lambda}(t)] \tag{61}$$

$$\bar{a}_{\lambda}(t) = \frac{1}{\sqrt{2\hbar\,\omega_{\lambda}}}\,[\omega_{\lambda}\, Q_{\lambda}(t) - iP_{\lambda}(t)] \tag{62}$$

Since $[\omega_{\lambda}\, Q_{\lambda}(t) + iP_{\lambda}(t)]$ is proportional to $q_{\lambda}(t)$ (see Eq. 54) which has a time dependence of the form $e^{-i\omega_{\lambda}t}$, we may write (cf. Eq. 112 of Chapter 8)

$$a_{\lambda}(t) = a_{\lambda}\, e^{-i\omega_{\lambda}t} \tag{63}$$

Similarly,

$$\bar{a}_{\lambda}(t) = \bar{a}_{\lambda}\, e^{+i\omega_{\lambda}t} \tag{64}$$

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[*] Notice that

$$\frac{\partial H_{\lambda}}{\partial Q_{\lambda}} = \omega_{\lambda}^2\, Q_{\lambda} = \omega_{\lambda}^2\,(\epsilon_0\, V)^{1/2}\,(q_{\lambda} + q_{\lambda}^*) = i\,(\epsilon_0\, V\omega_{\lambda}^2)^{1/2}\,(\dot{q}_{\lambda} - \dot{q}_{\lambda}^*) = -\,\dot{P}_{\lambda}$$

Similarly

$$\frac{\partial H_{\lambda}}{\partial P_{\lambda}} = +\,\dot{Q}_{\lambda}$$

which are nothing but Hamilton's equations of motion [see, e.g., Goldstein (1950)]. Thus Q_{λ} and P_{λ} are the canonical co-ordinates.

where

$$a_\lambda \equiv a_\lambda(0) \quad \text{and } \bar{a}_\lambda \equiv \bar{a}_\lambda(0) \tag{65}$$

Solving Eqs. (61) and (62) for $Q_\lambda(t)$ and $P_\lambda(t)$ we obtain

$$Q_\lambda(t) = \sqrt{\frac{\hbar}{2\omega_\lambda}}\,[\bar{a}_\lambda(t) + a_\lambda(t)] \tag{66}$$

$$P_\lambda(t) = i\left(\frac{\hbar\omega_\lambda}{2}\right)^{1/2}[\bar{a}_\lambda(t) - a_\lambda(t)]. \tag{67}$$

Substituting the above expressions for $Q_\lambda(t)$ and $P_\lambda(t)$ in Eq. (57), we obtain

$$\begin{aligned} H_r = \sum_\lambda H_\lambda &= \sum_\lambda{}' \frac{1}{2}\hbar\omega_\lambda[\bar{a}_\lambda(t)\ a_\lambda(t) + a_\lambda(t)\ \bar{a}_\lambda(t)] \\ &= \sum_\lambda \frac{1}{2}\hbar\omega_\lambda(\bar{a}_\lambda\ a_\lambda + a_\lambda\ \bar{a}_\lambda) \end{aligned} \tag{68}$$

If we now carry out an analysis similar to that followed in Sec. 8.9, we obtain

$$(n_\lambda + \tfrac{1}{2})\,\hbar\omega_\lambda; \quad n_\lambda = 0, 1, 2, \ldots. \tag{69}$$

as the eigenvalues of H_λ and

$$\sum_\lambda\left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda \tag{70}$$

as the eigenvalues of the total Hamiltonian $H_r\ (=\Sigma H_\lambda)$. Thus, quantum mechanically, we can visualize the radiation field as consisting of an infinite number of simple harmonic oscillators; the energy of each oscillator can increase or decrease by integral multiples of $\hbar\omega_\lambda$. If we consider $\hbar\omega_\lambda$ as the energy of a *photon*, each oscillator can have energy corresponding to n_λ photons.

The eigenkets of the total Hamiltonian would be

$$|n_1\rangle\,|n_2\rangle\,|n_3\rangle\cdots|n_\lambda\rangle\cdots = |n_1, n_2, n_3, \cdots n_\lambda, \cdots\rangle \tag{71}$$

where n_λ represents the number of photons in the mode characterized by λ. Thus

$$H_r\,|n_1, n_2, \ldots n_\lambda \ldots\rangle = \left(\sum_\lambda\left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda\right)|n_1, n_2, \ldots n_\lambda, \ldots\rangle \tag{72}$$

Further (see Eqs. 67 and 68 of Chapter 8):

$$a_\lambda\,|n_1, n_2, \ldots n^\lambda, \ldots\rangle = \sqrt{n_\lambda}\,|n_1, n_2, \ldots, n_\lambda - 1, \ldots.\rangle \tag{73}$$

$$\bar{a}_\lambda\,|n_1, n_2, \ldots n_\lambda, \ldots\rangle = \sqrt{n_\lambda + 1}\,|n_1, n_2, \ldots n_\lambda + 1, \ldots.\rangle \tag{74}$$

$$\langle n_1', n_2', \ldots n_, , \ldots | n_1, n_2, \ldots n_\lambda\rangle = \delta_{n_1, n_1'}\,\delta_{n_2, n_2'}\ldots\delta_{n_\lambda, n_\lambda'}, \ldots \tag{75}$$

Finally, the state of the radiation field need not be an eigenstate of H_r, it could be a superposition of the eigenstates like that given by the following equation

$$| \Psi \rangle = \sum_{n_1,\ldots} C_{n_1,n_2,\ldots n_\lambda,\ldots} \, | n_1, n_2, \ldots n_\lambda, \ldots \rangle \tag{76}$$

Physically $| C_{n_1,n_2,\ldots n_\lambda,\ldots} |^2$ would represent the probability of finding n_1 photons in the first mode, n_2 in the second mode; etc.

22.4 Spontaneous and Stimulated Emissions

We next express the vector potential A (and hence the interaction term H') in terms of the operators a_λ and $\bar{a}_\lambda$. Now using Eqs. (54) and (61), we get

$$q_\lambda(t) = \left(\frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} a_\lambda(t) \tag{77}$$

which is now to be considered as an operator. Using Eq. (38) we get

$$\begin{aligned} \mathbf{A} &= \sum_\lambda \left(\frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} [a_\lambda(t) \, A_\lambda(\mathbf{r}) + \bar{a}_\lambda(t) \, A_\lambda^*(\mathbf{r})] \\ &= \sum_\lambda \left(\frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} [a_\lambda(t) \, e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \bar{a}_\lambda(t) \, e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}] \end{aligned} \tag{78}$$

where all the operators are in the Heisenberg representation (see Sec. 8.12). In the Schrödinger representation, we will have

$$\mathbf{A} = \sum_\lambda \left(\frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} [a_\lambda \, e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \bar{a}_\lambda \, e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}] \hat{e}_\lambda \tag{79}$$

which will be independent of time. The interaction energy is given by

$$H' = \frac{q}{m} \mathbf{A} \cdot \mathbf{p} \tag{80}$$

or,

$$H' = \frac{q}{m} \sum_\lambda \left(\frac{\hbar}{2\epsilon_0 V \omega_\lambda} \right)^{1/2} [a_\lambda \, e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \bar{a}_\lambda \, e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}] \hat{e}_\lambda \cdot \mathbf{p} \tag{81}$$

Now, the eigenvalue equations for H_a and H_r are

$$H_a \, | \psi_i \rangle = E_i \, | \psi_i \rangle \tag{82}$$

and

$$H_r \, | n_1, n_2, \ldots \rangle = \left[\sum_\lambda \left(n_\lambda + \frac{1}{2} \right) \hbar\omega_\lambda \right] | n_1, n_2, \ldots n_\lambda, \ldots \rangle \tag{83}$$

where $| \psi_i \rangle$ and E_i represent respectively the eigenkets and energy eigenvalues of the isolated atom and $| n_1, n_2, \ldots \rangle$ represent the eigenket of the pure radiation field with $\sum_\lambda (n_\lambda + \frac{1}{2})\, \hbar\omega_\lambda$ representing the corresponding eigenvalue (see Eq. 72). Thus the eigenvalue equation for H_0 will be

$$H_0 \mid u_n\rangle = W_n \mid u_n\rangle \tag{84}$$

where

$$W_n = E_n + \Sigma\, (n_\lambda + \tfrac{1}{2})\, \hbar\omega_\lambda \tag{85}$$

and

$$\mid u_n\rangle = \mid i\rangle \mid n_1, n_2, \ldots n_\lambda, \ldots\rangle = \mid i; n_1, n_2 \ldots n_\lambda, \ldots\rangle \tag{86}$$

represents the ket corresponding to the atom being in state $\mid i\rangle$ and the radiation being in the state $\mid n_1, n_2, \ldots n_\lambda, \ldots\rangle$.

Now the Schrödinger equation for the system consisting of the atom and the radiation field is

$$i\hbar \frac{\partial \mid \Psi\rangle}{\partial t} = (H_0 + H') \mid \Psi\rangle \tag{87}$$

As in Sec. 20.2, the solution of the above equation can be written as a linear combination of the eigenkets of H_0 (cf. Eq. 15 of Chapter 21)

$$\mid \Psi\rangle = \sum_n C_n(t)\, e^{-iW_nt/\hbar} \mid u_n\rangle \tag{88}$$

Substituting in Eq. (87), we obtain

$$i\hbar \sum_n \left[\frac{dC_n}{dt} - i\,\frac{W_n C_n}{\hbar}\right] e^{-iW_nt/\hbar} \mid u_n\rangle = \sum_n C_n(t)\, W_n \exp(-iW_nt/\hbar) \mid u_n\rangle$$

$$+ H' \sum_n C_n(t) \exp(-iW_nt/\hbar) \mid u_n\rangle$$

where we have used Eq. (84). Premultiplying by $\langle u_s \mid$ we get (cf. Eq. 16 of Chapter 22)

$$i\hbar \frac{dC_s}{dt} = \sum_n \langle u_s \mid H' \mid u_n\rangle\, e^{i(W_m - W_n)t/\hbar}\, C_n(t) \tag{89}$$

Now using Eq. (81)

$$\langle u_s \mid H' \mid u_n\rangle = \frac{q}{m} \sum_\lambda \left(\frac{\hbar}{2\epsilon_0 V\omega_\lambda}\right)^{1/2} \hat{e}_\lambda \cdot \langle u_s \mid (a_\lambda\, e^{i\mathbf{k}_\lambda\cdot\mathbf{r}}$$

$$+ \bar{a}_\lambda\, e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}})\, \mathbf{p} \mid u_n\rangle \tag{90}$$

Because of the appearance of a_λ and $\bar{a}_\lambda$ in the expression for H', the various terms in $\langle u_s \mid H' \mid u_n\rangle$ will be non-zero only if the number of photons in $\mid u_s\rangle$ differs by unity from the number of photons in $\mid u_n\rangle$. If we write out completely the right hand side of Eq. (89) it will lead to a coupled set of an infinite number of equations which would be impossible to solve. We employ the perturbation theory and consider the absorption of one photon (of energy $\hbar\omega_i$) from the ith mode. Further, if we assume the frequency ω_i to be very close to the resonant frequency corresponding to the transition from the atomic state $|a\rangle$ to $|b\rangle$, then Eq. (89) reduces to the following two coupled equations (see also Solution 22.3)

$$i\hbar \frac{dC_1}{dt} = H'_{12} \exp\{i(W_1 - W_2)\, t/\hbar\}\, C_2(t) \tag{91}$$

$$i\hbar \frac{dC_2}{dt} = H'_{21} \exp\{-i(W_1 - W_2)\, t/\hbar\}\, C_1(t) \tag{92}$$

where

$$|1\rangle = |a; n_1, n_2, \ldots n_\lambda, \ldots n_i, \ldots\rangle \tag{93}$$

and

$$|2\rangle = |b; n_1, n_2, \ldots n_\lambda, \ldots n_i - 1, \ldots\rangle \tag{94}$$

represent the initial and final states of the system. Obviously, because of relations like Eq. (115), $H'_{11} = 0 = H'_{22}$. Further,

$$\left.\begin{aligned} W_1 &= E_a + \sum_{\substack{\lambda \\ \neq i}} \left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda + \left(n_i + \frac{1}{2}\right)\hbar\omega_i \\ &\text{and} \\ W_2 &= E_b + \sum_{\substack{\lambda \\ \neq i}} \left(n_\lambda + \frac{1}{2}\right)\hbar\omega_\lambda + \left(n_i - 1 + \frac{1}{2}\right)\hbar\omega_i \end{aligned}\right\} \tag{95}$$

Thus,

$$W_1 - W_2 = (E_a - E_b) + \hbar\omega_i \tag{96}$$

Now

$$\begin{aligned} H'^{*}_{21} = H'_{12} &= \sum_\lambda \frac{q}{m}\left(\frac{\hbar}{2\epsilon_0 V\omega_\lambda}\right)^{1/2} \hat{e}_\lambda \cdot \langle a; n_1, n_2, \ldots n_i, \ldots | \\ &\qquad (a_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}})\, \mathbf{p}\, | b; n_1, n_2, \ldots n_i - 1, \ldots\rangle \\ &= \frac{q}{m}\left(\frac{\hbar}{2\epsilon_0 V\omega_i}\right)^{1/2} \sqrt{n_i}\, \hat{e}_\lambda \cdot \langle a | e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\, \mathbf{p} | b\rangle \\ &\simeq \frac{q}{m}\left(\frac{\hbar}{2\epsilon_0 V\omega_i}\right)^{1/2} \sqrt{n_i}\, \hat{e}_\lambda \cdot \langle a | \mathbf{p} | b\rangle \end{aligned} \tag{97}$$

where in the last step we have used the dipole approximation in which we have replaced $e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}$ by unity (see Eq. 14). If we now use Eq. (19) we get

$$\begin{aligned}\langle a\,|\,\mathbf{p}\,|\,b\rangle &= \frac{m}{i\hbar}\,(E_b - E_a)\,\langle a\,|\,\mathbf{r}\,|\,b\rangle\\ &= -im\,\omega_{ba}\,\langle a\,|\,\mathbf{r}\,|\,b\rangle\end{aligned}$$

Thus

$$H_{21}^{\prime *} = H_{12}^{\prime} = -i\left(\frac{\hbar}{2\epsilon_0 V\omega_i}\right)^{1/2}\omega_{ba}\sqrt{n_i}\,\mathcal{D}_{ab} \tag{98}$$

where

$$\mathcal{D}_{ab} = q\hat{\mathbf{e}}_\lambda\cdot\langle a\,|\,\mathbf{r}\,|\,b\rangle = \frac{iq}{m\omega_{ba}}\,\hat{\mathbf{e}}_\lambda\cdot\langle a\,|\,\mathbf{p}\,|\,b\rangle \tag{99}$$

(see Eq. 20 of Chapter 21). We next try to solve Eqs. (91) and (92) by using a method similar to that employed in Problem 21.8. We assume that at $t = 0$ the system is in the state represented by $|\,1\rangle$, i.e.

$$C_1(0) = 1,\quad C_2(0) = 0 \tag{100}$$

On working out the solution we obtain

$$|\,C_2(t)\,|^2 \simeq \left(\frac{\Omega_0}{2}\right)^2\left[\frac{\sin\Omega' t/2}{\Omega'/2}\right]^2 \tag{101}$$

where

$$\Omega_0 = \left[\frac{2n_i\,|\,\mathcal{D}_{ab}\,|^2}{\hbar\epsilon_0 V}\quad\frac{\omega_{ab}^2}{\omega_i}\right]^{1/2} \tag{102}$$

and

$$\Omega' = [(\omega_{ba} - \omega_i)^2 + \Omega_0^2]^{1/2} \tag{103}$$

For $\Omega_0 t/\hbar \ll 1$, we obtain

$$|\,C_2(t)\,|^2 \simeq \frac{n\omega\,|\,\mathcal{D}_{ab}\,|^2}{2\hbar\epsilon_0 V}\left[\frac{\sin(\omega_{ba} - \omega)t/2}{(\omega_{ba} - \omega)/2}\right]^2 \tag{104}$$

where we have dropped the subscript i and have taken into account the fact that $|\,C_2(t)\,|^2$ is negligible except when $\omega \approx \omega_{ba}$ and have thus replaced ω_{ba} by ω. Equation (104) is the same as Eq. (24) of the previous chapter provided we replace[*] $\mathcal{E}_0^2$ by $2n\hbar\omega/V$. Using Eq. (104) and proceeding as in Sec. 21.4, we would get an expression for the Einstein B coefficient identical to Eq. (40) of Chapter 21.

In a similar manner, if we consider the emission process, we would obtain

$$|\,C_2(t)\,|^2 \simeq \frac{\omega(n+1)}{2\hbar\epsilon_0 V}\left|\,\mathcal{D}_{ab}\right|^2\left[\frac{\sin(\omega_{ba} - \omega)t/2}{(\omega_{ba} - \omega)/2}\right]^2 \tag{105}$$

---

[*] This is justified because the energy density associated with an electromagnetic field is $\frac{1}{2}\epsilon_0\,\mathcal{E}_0^2$ and the energy density is also equal to $n\hbar\omega/V$.

where the initial and final states $|\,1\rangle$ and $|\,2\rangle$ are now given by[*]

$$\left.\begin{aligned} |\,\text{initial}\rangle &= |\,1\rangle = |\,b; n_1, n_2, \ldots n_i, \ldots\rangle \\ |\,\text{final}\;\rangle &= |\,2\rangle = |\,a; n_1, n_2, \ldots n_i + 1, \ldots\rangle \end{aligned}\right\} \tag{106}$$

Notice the presence of the term[**] $(n + 1)$ in Eq. (105). This implies that even if the number of photons were zero originally, the emission probability in finite. The term proportional to n in Eq. (105) gives the probability for induced or stimulated emission since the rate at which it occurs is proportional to the intensity of the applied radiation. On the other hand, the second term which is independent of n gives the spontaneous emission rate into the mode (see also Problem 22.3). It may be noted that the spontaneous emission probability into a particular mode is exactly the same as the stimulated emission probability caused by a single photon into the same mode.

We next calculate the probability per unit time for spontaneous emission of radiation. If we consider the emission to be in the solid angle $d\Omega$ then the number of modes for which the photon frequency lies between ω and $\omega + d\omega$ is (see Appendix M)

$$N(\omega)\, d\omega\, d\Omega = \frac{V\omega^2\, d\omega}{8\pi^3 c^3}\, d\Omega \tag{107}$$

Thus, the total probability of emission in the solid angle $d\Omega$ would be given by

$$\begin{aligned} \Gamma &= \frac{|\,\mathcal{D}_{ab}\,|^2}{2\hbar\epsilon_0 V} \int \left[\frac{\sin[\omega_{ba} - \omega]t/2}{(\omega_{ba} - \omega)/2}\right]^2 \omega\, \frac{V}{8\pi^3 c^3}\, \omega^2\, d\omega\, d\Omega \\ &\simeq \frac{|\,\mathcal{D}_{ab}\,|^2}{2\hbar\epsilon_0\, 8\pi^3 c^3}\, d\Omega\, \omega_{ba}^3 \int \left[\frac{\sin(\omega_{ba} - \omega)t/2}{(\omega_{ba} - \omega)/2}\right]^2 d\omega \end{aligned} \tag{108}$$

where use has been made of the fact that the quantity inside the square brackets is a sharply peaked function around $\omega = \omega_{ba}$. Using the relation

$$\int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2}\, dx = \pi$$

we obtain

$$\Gamma \simeq \frac{1}{2\pi}\left[\frac{q^2}{4\pi\,\epsilon_0\,\hbar c}\right] \frac{\omega^3}{c^2}\, |\langle a\,|\,\mathbf{r}\,|\,b\rangle \cdot \hat{\mathbf{e}}\,|^2\, d\Omega\, t$$

---

[*] We would have

$$i\hbar\frac{dC_2}{dt} \simeq H'_{21} \exp[-i\,(W_1 - W_2)t/\hbar\, C_1(t) \simeq H'_{21} \exp[-i(\omega_{ba} - \omega_i)\, t]$$

and integration of which would lead to Eq. (105). However, it may be mentioned that the equation for $C_1(t)$ would be a sum over states as discussed in Solution 22.3.

[**] The appearance of the term $(n + 1)$ is because of the relation $|\,\langle n + 1\,|\,\bar{a}\,|\,n\rangle\,|^2 = |\,\sqrt{n+1}\,\langle n + 1\,|\,n + 1\rangle\,|^2 = (n + 1)$.

Thus the transition rate is given by

$$w_{sp} = \frac{1}{2\pi}\left[\frac{q^2}{4\pi\epsilon_0\hbar c}\right]\frac{\omega}{m^2c^2}\,|\langle a\,|\,\mathbf{p}\,|\,b\rangle\cdot\hat{\mathbf{e}}\,|^2\,d\Omega \tag{109}$$

$$= \frac{1}{2\pi}\left[\frac{q^2}{4\pi\epsilon_0\hbar c}\right]\frac{\omega^2}{c^2}\,|\langle a\,|\,\mathbf{r}\,|\,b\rangle\cdot\hat{\mathbf{e}}\,|^2\,d\Omega \tag{110}$$

In order to calculate the total probability per unit time for the spontaneous emission to occur (the inverse of which will give the spontaneous lifetime of the state), we must sum over the independent states of polarization and integrate over the solid angle. Assuming the direction of $\mathbf{k}$ to be along the z-axis, we may choose $\mathcal{E}$ to be along the x or y axes. Thus, if we sum

$$|\langle b\,|\,\mathbf{r}\,|\,a\rangle\cdot\hat{\mathbf{e}}\,|^2$$

over the two independent states of polarization, we obtain

$$|\langle b\,|\,\mathbf{r}\,|\,a\rangle\cdot\hat{\mathbf{x}}\,|^2 + |\langle b\,|\,\mathbf{r}\,|\,a\rangle\cdot\mathbf{y}\,|^2$$
$$= P_x^2 + P_y^2 = P^2\sin^2\theta$$

where $\mathbf{P} \equiv \langle b\,|\,\mathbf{r}\,|\,a\rangle$ and θ is the angle that $\mathbf{P}$ makes with the z-axis. Thus in order to obtain the Einstein A coefficient (which represents the total probability per unit time for the spontaneous emission to occur), in Eq. (110), we replace $|\langle b\,|\,\mathbf{r}\,|\,a\rangle\cdot\hat{\mathbf{e}}\,|^2$ by $|\langle b\,|\,\mathbf{r}\,|\,a\rangle\,|^2\sin^2\theta$ and integrate over the solid angle $d\Omega$ to obtain

$$A = \frac{1}{2\pi}\left[\frac{q^2}{4\pi\epsilon_0\hbar c}\right]\frac{\omega^3}{c^2}\,|\langle b\,|\,\mathbf{r}\,|\,a\rangle\,|^2\iint\sin^2\theta\sin\theta\,d\theta\,d\varphi$$

$$= \frac{4}{3}\left[\frac{q^2}{4\pi\epsilon_0\hbar c}\right]\frac{\omega^3}{c^2}\,|\langle b\,|\,\mathbf{r}\,|\,a\rangle\,|^2 \tag{111}$$

which is identical to Eq. (42) of the previous chapter.

22.5 Properties of the Eigenstates of the Hamiltonian of the Radiation Field

If we substitute for $q_\lambda(t)$ from Eq. (77) in Eq. (44) we would obtain

$$\mathcal{E} = \sum_\lambda \mathcal{E}_\lambda \tag{112}$$

where

$$\mathcal{E}_\lambda = i\left(\frac{\hbar\omega_\lambda}{2\epsilon_0 V}\right)^{1/2}[a_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} - \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}]\,\hat{\mathbf{e}}_\lambda \tag{113}$$

and all operators are in the Schrödinger representation. We consider the state of the radiation field for which there are n_λ photons in the state λ. The expectation value of $\mathcal{E}_\lambda$ in this state would be given by

$$\langle n_1, n_2, \ldots n_\lambda, \ldots\,|\,\mathcal{E}_\lambda\,|\,n_1, n_2, \ldots n_\lambda, \ldots\rangle = \langle n_1\,|\,n_1\rangle\langle n_2\,|\,n_2\rangle\ldots$$
$$\langle n_\lambda\,|\,\mathcal{E}_\lambda\,|\,n_\lambda\rangle\ldots = 0 \tag{114}$$

because

$$\langle n_\lambda \mid a_\lambda \mid n_\lambda \rangle = 0 = \langle n_\lambda \mid \bar{a}_\lambda \mid n_\lambda \rangle \tag{115}$$

Similarly

$$\begin{aligned}\langle n_1, n_2, \ldots n_\lambda \ldots \mid \mathcal{E}_\lambda^2 \mid n_1, n_2, \ldots n_\lambda \ldots \rangle &= \langle n_1 \mid n_1 \rangle \langle n_2 \mid n_2 \rangle \ldots \\ &\quad \ldots \langle n_\lambda \mid \mathcal{E}_\lambda^2 \mid n_\lambda \rangle \ldots \\ &= -\left(\frac{\hbar\omega_\lambda}{2\epsilon_0 V}\right) \langle n_\lambda \mid (a_\lambda\, e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} - \bar{a}_\lambda\, e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}})\,(a_\lambda\, e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}} - \bar{a}_\lambda\, e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}) \mid n_\lambda \rangle \\ &= \left(\frac{\hbar\omega_\lambda}{\epsilon_0 V}\right)\left(n_\lambda + \frac{1}{2}\right)\end{aligned} \tag{116}$$

where use has been made of relations like (see Sec. 8.9)

$$\langle n_\lambda \mid a_\lambda \bar{a}_\lambda \mid n_\lambda \rangle = \sqrt{n_\lambda + 1}\,\langle n_\lambda \mid a_\lambda \mid n_\lambda + 1 \rangle = (n_\lambda + 1) \tag{117}$$

$$\langle n_\lambda \mid \bar{a}_\lambda a_\lambda \mid n_\lambda \rangle = \sqrt{n_\lambda}\,\langle n_\lambda \mid \bar{a}_\lambda \mid n_\lambda - 1 \rangle = n_\lambda \tag{118}$$

$$\langle n_\lambda \mid a_\lambda a_\lambda \mid n_\lambda \rangle = 0 \tag{119}$$

$$\langle n_\lambda \mid \bar{a}_\lambda \bar{a}_\lambda \mid n_\lambda \rangle = 0 \tag{120}$$

The uncertainty in $\mathcal{E}_\lambda$, $\Delta\mathcal{E}_\lambda$, can be defined through the relation

$$\begin{aligned}(\Delta\mathcal{E}_\lambda)^2 &= \langle \mathcal{E}_\lambda^2 \rangle - \langle \mathcal{E}_\lambda \rangle^2 \\ &= \left(\frac{\hbar\omega_\lambda}{\epsilon_0 V}\right)\left(n_\lambda + \frac{1}{2}\right)\end{aligned} \tag{121}$$

Equation (114) tells us that the expectation value of the electric field in the state $\mid n \rangle$ ($= \mid n_1, n_2, \ldots n_\lambda \ldots \rangle$) is zero. Since the average of sine waves with random phases is zero, we may *loosely* say that the state $\mid n \rangle$ does not specify the phase*. Some authors tend to explain this by resorting to the uncertainty principle

$$\Delta E\, \Delta t \geqslant \hbar \tag{122}$$

where ΔE is the uncertainty in the energy of the radiation field and Δt is related to the uncertainty in the phase angle through the relation

$$\Delta\phi = \omega \Delta t \tag{123}$$

Since $E = (n + \frac{1}{2})\hbar\omega$, $\Delta E = \hbar\omega\Delta n$ and we obtain

$$\Delta n\, \Delta\phi \geqslant 1 \tag{124}$$

If the number of photons is exactly known, then $\Delta n = 0$ and consequently there is no knowledge of the phase. However, such arguments are not rigorously correct because it is not possible to give a precise definition of $\Delta\phi$ (see Sec. 22.7). Nevertheless, we can say that the states described by $\mid n \rangle$ do not correspond to the classical electromagnetic wave with a certain phase.

---

*We say it loosely because it is not possible to define a phase operator which is real (see Sec. 22.7).

Returning to Eq. (116), we notice that the states $|\, n\rangle$ have a definite amplitude $(2\hbar\omega_\lambda/\epsilon_0 V)^{1/2}\,(n_\lambda + \frac{1}{2})^{1/2}$ for the mode λ which is directly related to the number of photons.

22.6 The Coherent States

We next consider the radiation field to be in one of the coherent states which are, the eigenkets of the operator a_λ (see Sec. 8.9.3). We will show that when the radiation field is in a coherent state, the field has properties very similar to that of a classical electromagnetic wave with a certain phase and amplitude. However, before we do so, we would like to discuss some of the properties of the coherent states.

The coherent states satisfy the equation

$$a_\lambda \,|\, \alpha_\lambda\rangle = \alpha_\lambda \,|\, \alpha_\lambda\rangle \tag{125}$$

where α_λ, which represents the eigenvalues of a_λ, can be an arbitrary complex number. In Sec. 8.9.3 we had shown that

$$|\, \alpha_\lambda \rangle = \exp\left[-\frac{1}{2}\left|\alpha_\lambda\right|^2\right] \sum_{n_\lambda=0,1,2,\ldots} \frac{\alpha_\lambda^{n_\lambda}}{n_\lambda!}\,|\, n_\lambda\rangle$$

For convenience, we drop the subscript λ and write the above equation as

$$|\, \alpha\rangle = \exp\left[-\frac{N}{2}\right] \sum_{n} \frac{\alpha^n}{\sqrt{n!}}\,|\, n\rangle \tag{126}$$

where $N(=|\,\alpha\,|^2)$ represents the expectation value of the number operator N_{op} (see Problem 22.4). Since $|\, n\rangle$ are eigenkets of H, if the field is in the coherent state at $t = 0$, then at a later time t, the state will be given by (see Eq. 11 of Chapter 3)

$$|\, \Psi(t)\rangle = e^{-N/2} \sum_{n} \frac{\alpha^n}{\sqrt{n!}} \exp\left[-i(n + \tfrac{1}{2})\omega t\right] |\, n\rangle \tag{127}$$

It is easy to see that

$$|\, \Psi(0)\rangle = |\, \alpha\rangle$$

Further*

$$\begin{aligned}\langle \Psi(t)\,|\, \bar{a}\,|\, \Psi(t)\rangle &= e^{-N} \sum_{m}\sum_{n} \frac{\alpha^{*m}\,\alpha^n}{\sqrt{m!\,n!}}\, e^{i(m-n)\omega t} \sqrt{n+1}\,\langle m\,|\, n+1\rangle \\ &= e^{i\omega t}\, e^{-N} \sum \frac{\alpha^*\,|\,\alpha\,|^{2n}}{n!} = \alpha^*\, e^{i\omega t}\end{aligned} \tag{128}$$

---

*In the Heisenberg representation, the expectation value of $\bar{a}$ would have been

$$\langle \Psi(0)\,|\, \bar{a}(t)\,|\, \Psi(0)\rangle = \langle \alpha\,|\, \bar{a}\, e^{i\omega t}\,|\, \alpha\rangle = \alpha^*\, e^{i\omega t}$$

which is the same as expressed by Eq. (128).

Similarly, or taking the complex conjugate of Eq. (128)

$$\langle \Psi(t) \mid a \mid \Psi(t) \rangle = \alpha e^{-i\omega t} \tag{129}$$

We now consider the radiation field to be in the coherent state and calculate the expectation value of $\mathcal{E}$ and $\mathcal{E}^2$

$$\begin{aligned} \langle \Psi(t) \mid \mathcal{E} \mid \Psi(t) \rangle &= i\left(\frac{\hbar\omega}{2\epsilon_0 V}\right)^{1/2} [\langle \Psi(t) \mid a \mid \Psi(t) \rangle\, e^{i\mathbf{k}\cdot\mathbf{r}} \\ &\qquad - \langle \Psi(t) \mid \bar{a} \mid \Psi(t) \rangle\, e^{-i\mathbf{k}\cdot\mathbf{r}}]\, \hat{\mathbf{e}} \\ &= i\left(\frac{\hbar\omega}{2\epsilon_0 V}\right)^{1/2} [\alpha e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} - \alpha^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}]\, \hat{\mathbf{e}} \\ &= -2\left(\frac{\hbar\omega}{2\epsilon_0 V}\right)^{1/2} \mid \alpha \mid \sin(\mathbf{k}\cdot\mathbf{r} - \omega t + \varphi)\, \hat{\mathbf{e}} \end{aligned} \tag{130}$$

where

$$\alpha = \mid \alpha \mid e^{i\varphi} \tag{131}$$

Thus the coherent state can be interpreted to represent a harmonic wave with phase φ. In a similar manner, we can calculate the expectation value $\mathcal{E}^2$. The result is

$$\langle \Psi(t) \mid \mathcal{E}\cdot\mathcal{E} \mid \Psi(t) \rangle = \left(\frac{\hbar\omega}{2\epsilon_0 V}\right)[4 \mid \alpha \mid^2 \sin^2(\mathbf{k}\cdot\mathbf{r} - \omega t + \varphi) + 1] \tag{132}$$

Finally, the uncertainty in $\mathcal{E}$ would be given by (cf. Eq. 121):

$$\begin{aligned} (\Delta\mathcal{E})^2 &= \langle \Psi(t) \mid \mathcal{E}^2 \mid \Psi(t) \rangle - \langle \Psi(t) \mid \mathcal{E} \mid \Psi(t) \rangle^2 \\ &= \left(\frac{\hbar\omega}{2\epsilon_0 V}\right) \end{aligned} \tag{133}$$

Notice that the uncertainty $\Delta\mathcal{E}$ is independent of the amplitude $\mid \alpha \mid$; thus, greater the intensity of the beam greater will be the proximity of the radiation field (corresponding to the coherent state) to the classical plane wave. Indeed when a laser is operated much beyond the threshold, it generates a coherent state excitation of a cavity mode.

22.7 The Phase Operator

In classical mechanics the displacement and momentum of a linear harmonic oscillator are given by

$$x = Ae^{i\phi} + Ae^{-i\phi}, \quad \phi = \omega t \tag{134}$$

and

$$p = m\dot{x} = im\,\omega A[e^{i\phi} - e^{-i\phi}] \tag{135}$$

where A has been assumed to be real. In quantum mechanics, we have (see

Eqs. 71 and 72 of Chapter 8):

$$x = \left(\frac{2\hbar}{m\omega}\right)^{1/2} [\bar{a} + a] \tag{136}$$

$$p = im\,\omega \left(\frac{2\hbar}{m\omega}\right)^{1/2} [\bar{a} - a] \tag{137}$$

The above four equations suggest the phase operator ϕ to be defined through the following equations

$$\bar{a} = Re^{i\phi} \tag{138}$$

and $$a = e^{-i\phi}R \tag{139}$$

where R and ϕ are assumed to be Hermitian operators (see, e.g., Dirac, 1958; Heitler, 1954). However, such a definition will lead to inconsistent results as discussed below. Now, the number operator is given by

$$N_{op} = \bar{a}a = Re^{i\phi}\, e^{-i\phi}\, R = R^2$$

or

$$R = N_{op}^{\frac{1}{2}} \tag{140}$$

where the square root of an operator is defined through the relation

$$N_{op} = N_{op}^{\frac{1}{2}}\, N_{op}^{\frac{1}{2}}$$

Since

$$[a, \bar{a}] = a\bar{a} - \bar{a}a = 1$$

so,

$$e^{-i\phi}\, RRe^{i\phi} - Re^{i\phi}\, e^{-i\phi}\, R = 1$$

or, premultiplying by $e^{i\phi}$, we get

$$N_{op}\, e^{i\phi} - e^{i\phi}\, N_{op} = e^{i\phi} \tag{141}$$

The above equation is satisfied if ϕ and N_{op} satisfy the commutation relation*

$$[N_{op}, \phi] = N_{op}\,\phi - \phi\, N_{op} = -i \tag{142}$$

Thus $$\langle m \mid N_{op}\,\phi - \phi\, N_{op} \mid n \rangle = -i \langle m \mid n \rangle = -i\delta_{mn}$$

or, $$(m - n) \langle m \mid \phi \mid n \rangle = -i\delta_{mn} \tag{143}$$

*This follows from the repeated application of Eq. (142) which gives

$$N_{op}\,\phi^m - \phi^m\, N_{op} = -im\,\phi^{m-1}$$

Now

$$[N_{op}, e^{i\phi}] = \sum_m \frac{i^m}{m!}[N_{op}, \phi^m] = \sum_m \frac{i^{m-1}\phi^{m-1}}{(m-1)!} = e^{i\phi}$$

which is certainly an impossibility! Thus the definition of a Hermitian ϕ through Eq. (138) leads to inconsistent results.

PROBLEMS

PROBLEM 22.1

Consider the matrix element $\langle s \mid e^{-i\mathbf{k}\cdot\mathbf{r}}\,\hat{\mathbf{e}}\cdot\mathbf{p} \mid n\rangle$ (see Eq. 13). Since in many cases of interest $kR \ll 1$ (where R represents the dimension of the system), we may write

$$e^{-i\mathbf{k}\cdot\mathbf{r}} = 1 - i\,\mathbf{k}\cdot\mathbf{r} - \frac{(\mathbf{k}\cdot\mathbf{r})^2}{2!} + \dots \tag{144}$$

It can be shown that the term $(\mathbf{k}\cdot\mathbf{r})^n$ gives the electric 2^{n+1} pole and the magnetic 2^n pole transitions. Verify this statement for the case $n = 1$.

PROBLEM 22.2

Obtain the selection rules for allowed transitions of a linear harmonic oscillator. Calculate the lifetime of an oscillator in the first excited state.

PROBLEM 22.3

Show that the frequency distribution of the emitted radiation from an isolated atom is given by the natural line shape function

$$f(\omega)\,d\omega = \frac{K\,d\omega}{(\omega_0 - \omega)^2 + A^2/4} \tag{145}$$

where A represents the Einstein coefficient.

PROBLEM 22.4

Prove that the average number of photons in a coherent state is $|\alpha|^2$, i.e.

$$N \equiv \langle \alpha \mid N_{op} \mid \alpha\rangle = |\alpha|^2 \tag{146}$$

PROBLEM 22.5

Show that the probability of finding n photons in a coherent state is a Poisson distribution* about the mean $|\alpha|^2$

$$|\langle n \mid \alpha\rangle|^2 = \frac{N^n e^{-N}}{n!} \tag{147}$$

where $N\ (=|\alpha|^2)$ is defined in the previous problem.

---

*The photon counting experiment is of considerable importance in determining statistical properties of the light source. In a typical experiment, the light beam is allowed to fall on a phototube for a specific time interval T by having a shutter open in front of the detector for time T and one registers the number of photoelectrons so liberated. Then the shutter is again opened for an equal time interval T after a certain time delay and the experiment is repeated a large number of times. From the experiment one obtains the probability distribution of counting n photons in time T. From this one can derive the statistical properties of the source (see, e.g. Arecchi, 1970).

PROBLEM 22.6

Prove that the uncertainty in the number of photons in a coherent state is $\sqrt{N}$, i.e.,

$$\Delta N \equiv [\langle \alpha \mid N_{op}^2 \mid \alpha \rangle - (\langle \alpha \mid N_{op} \mid \alpha \rangle)^2] = N^{1/2} \tag{148}$$

Thus the fractional uncertainty in the average of photons $\Delta N/N (= 1/\sqrt{N})$ goes to zero with increase in intensity. It may be worthwhile pointing out that even in nuclear counting, the uncertainty in the actual count is $N^{1/2}$ (see, e.g., Bleuler and Goldsmith, 1952).

PROBLEM 22.7

Show that for $\mid \Psi(t) \rangle$ given by Eq. (127)

$\langle \Psi(t) \mid N_{op} \mid \Psi(t) \rangle = N$ (independent of time).

PROBLEM 22.8

Obtain an expression for the photodisintegration of the deuteron in the electric dipole approximation. Assume that the wavefunction of the deuteron may be approximated by

$$\psi = \sqrt{\frac{K}{2\pi}} \frac{e^{-Kr}}{r} \tag{149}$$

where $\hbar K = (2\mu B)^{1/2}$, $\mu = \frac{1}{2} M$ is the reduced mass of the system, $B = 2.2$ MeV is the binding energy. Neglect the interaction between neutron and proton in the final state [*Hint*: Use the Golden rule].

PROBLEM 22.9

(*a*) Derive the Thomas-Reiche-Kuhn sum rule

$$\sum_s (E_s - E_n) \mid \langle s \mid x \mid n \rangle \mid^2 = \frac{\hbar^2}{2m} \tag{150}$$

(*b*) Using the above sum rule show that for dipole transitions

$$\int \sigma \, dE = 2\pi^2 \alpha \hbar^2/m \tag{151}$$

PROBLEM 22.10

If the quantum energy $\hbar\omega$ of light falling on an atom is greater than the ionization energy, I, of the atom, the electron is raised into a state of continuous spectrum. In this case light of all frequencies can be absorbed, and the absorption spectrum is continuous. The kinetic energy T of the electron after leaving the atom is determined by Einstein's equation

$$T = \hbar\omega - I \tag{152}$$

Show that for the incident radiation polarized with its electric vector along $\hat{\mathbf{e}}$, the photoelectric absorption cross-section of an atom, for the ejection of an electron from the K-shell, is given by

$$\frac{d\sigma}{d\Omega} = \frac{32\,\hbar k}{m\omega}\left(\frac{q^2}{4\pi\epsilon_0\hbar c}\right)(\hat{\mathbf{e}}\cdot\mathbf{k})^2\left(\frac{Z}{a_0}\right)^5\left[\left(\frac{Z}{a_0}\right)^2 + q^2\right]^4 \tag{153}$$

where $\mathbf{k}$ is the wave vector of the ejected electron, $\mathbf{q}$ is the momentum transferred to the atom in units of $\hbar$

$$\mathbf{q} = \mathbf{k} - \frac{\omega}{c}\,\hat{\mathbf{n}} \tag{154}$$

$\hat{\mathbf{n}}$ is the unit vector along the direction of propagation. Assume $\hbar\omega \gg I$. [Use the Golden rule.]

SOLUTIONS

SOLUTION 22.1

The relevant term in the matrix element is

$$M = \langle s \mid (i\,\mathbf{k}\cdot\mathbf{r})\,(\hat{\mathbf{e}}\cdot\mathbf{p}) \mid n\rangle \tag{155}$$

Let us assume that the photon moves along the x-direction, and the polarization $\hat{\mathbf{e}}$ is along the z-direction. Thus

$$M = \langle s \mid ikx\,p_z \mid n\rangle = ik\,\langle s \mid x\,p_z \mid n\rangle$$

We write xp_z as

$$xp_z = \tfrac{1}{2}\,[xp_z + zp_x] + \tfrac{1}{2}\,[xp_z - zp_x]$$

Now, according to Eq. (17)

$$p_z = \frac{m}{i\hbar}\,[zH_a - H_a z]$$

Thus

$$xp_z = \frac{m}{i\hbar}\,[xzH_a - xH_a z]$$

Similarly

$$zp_x = p_x z = \frac{m}{i\hbar}\,[xH_a - H_a x]\,z$$

So that

$$\frac{1}{2}\,(xp_z + zp_x) = \frac{m}{2i\hbar}\,[xzH_a - H_a xz] \tag{156}$$

and

$$\tfrac{1}{2}\,(xp_z - zp_x) = -\tfrac{1}{2}\,L_y \tag{157}$$

where L_y is the y-component of the angular momentum. Thus

$$M = -ik \langle s \mid \frac{m}{2i\hbar}(H_a xz - xz H_a) + \tfrac{1}{2} L_y \mid n \rangle$$

$$= -\frac{m}{2\hbar}(E_s - E_n) \langle s \mid xz \mid n \rangle - \tfrac{1}{2} ik \langle s \mid L_y \mid n \rangle \tag{158}$$

The first term is the electric quadrupole term while the second is the magnetic dipole term (the magnetic moment is related to the angular momentum).

Solution 22.2

The relevant matrix element for allowed transition is

$$M = \langle m \mid x \mid n \rangle$$

The only non-vanishing matrix elements correspond to $m = n \pm 1$ (see Eqs. 67 and 68 of Chapter 8) and the values are given by

$$\left.\begin{aligned} \langle n+1 \mid x \mid n \rangle &= \sqrt{\frac{\hbar}{2m\omega}}\, \sqrt{n+1} \\ \text{and} \qquad & \\ \langle n-1 \mid x \mid n \rangle &= \sqrt{\frac{\hbar}{2m\omega}}\, \sqrt{n} \end{aligned}\right\} \tag{159}$$

Thus the selection rule is $\Delta n = \pm 1$. The transition rate is given by (see Eq. 109)

$$w_{sp} = \frac{1}{2\pi}\left[\frac{q^2}{4\pi\epsilon_0 \hbar c}\right]\frac{\omega}{m^2c^2} \mid \langle 0 \mid p_x \mid 1 \rangle \mid^2 d\Omega \tag{160}$$

Now

$$\langle 0 \mid p_x \mid 1 \rangle = -i\sqrt{\frac{m\hbar\omega}{2}} \tag{161}$$

(see Eq. 191 of Chapter 8). Thus the integrated rate over the whole solid angle is

$$\frac{1}{\tau} = \frac{\alpha\hbar\omega^2}{mc^2} \tag{162}$$

which gives the mean life τ; here α ($\simeq 1/137$) is the fine structure constant.

Solution 22.3

A spontaneous transition from a state b to a lower energy state a does not give radiation at a single frequency ω_{ba}. A finite lifetime τ of the excited state gives it an energy width of the order $\hbar/\tau$ so that the emitted radiation has a frequency distribution. This argument may be made more precise by considering the simple case of an atom with only 2 states a and b ($E_b > E_a$) undergoing spontaneous transition from b to a. We will calculate here the frequency distribution of the emitted radiation from such a spontaneous transition; the analysis is based on the treatment given by Heitler (1954), Chapter 18, and is known as Weisskopf-Wigner theory of the natural line width.

It is assumed that at $t = 0$, the atom is in the excited state b and the radiation field has no photons. We denote this state by

$$| 1 \rangle = | b; 0, 0, 0, \ldots \rangle$$

(see Eq. 93). The atom makes a transition to the state a emitting a photon of frequency ω_λ in the mode characterized by λ (see Eq. 71). We denote this state by

$$| a\lambda \rangle = | a; 0, 0, \ldots, 1_\lambda, 0 \ldots \rangle$$

If we denote the corresponding probability amplitudes by

$$C_1(t) \quad \text{and} \quad C_{a\lambda}(t) \qquad \text{then}$$

$$\text{and} \quad \left.\begin{aligned} C_1(0) &= 1 \\ C_{a\lambda}(0) &= 0 \end{aligned}\right\} \tag{163}$$

Further (see Eqs. 89-92)

$$\begin{aligned} i\hbar \frac{dC_1}{dt} &= \sum_\lambda \langle 1 \,|\, H' \,|\, a\lambda \rangle \exp[i(W_1 - W_{a\lambda})t/\hbar]\, C_{a_\lambda}(t) \\ &= \sum_\lambda \langle 1 \,|\, H' \,|\, a\lambda \rangle \exp[i(\omega_0 - \omega_\lambda)t]\, C_{a\lambda}(t) \end{aligned} \tag{164}$$

and

$$i\hbar \frac{dC_{a_\lambda}}{dt} = \langle a_\lambda \,|\, H' \,|\, 1 \rangle \exp[-i(\omega_0 - \omega_\lambda)t]\, C_1(t) \tag{165}$$

where

$$\hbar\omega_0 = E_b - E_a \tag{166}$$

and

$$W_1 - W_{a_\lambda} = E_b - (E_a + \hbar\omega_\lambda) = \hbar(\omega_0 - \omega_\lambda) \tag{167}$$

We try to solve Eqs. (164) and (165) by assuming*

$$C_1(t) = e^{-\gamma t/2} \tag{168}$$

---

*It should be mentioned that the present treatment is consistent with the treatment given in Sec. 22.4. Indeed, there we have shown that A (as given by Eq. 111) represents the probability for unit time for the spontaneous emission to occur from which the decay given by Eq. (108) follows with $\gamma = A$; this is explicitly shown later (see Eqs. 178 and 179).

which satisfies the condition $C_1(0) = 1$. It may be noted that since $|C_1(t)|^2$ represents the probability of finding the atom in the upper state, the quantity $1/\gamma$ represents the mean lifetime of the state. If we substitute for $C_1(t)$ in Eq. (165) and carry out the integration we get

$$C_{a_\lambda}(t) = \frac{\langle a\lambda \mid H' \mid 1 \rangle}{\hbar} \; \frac{\exp\{-[i(\omega_0 - \omega_\lambda) + \gamma/2]t\} - 1}{(\omega_0 - \omega_\lambda) - i(\gamma/2)} \tag{169}$$

We substitute Eqs. (168) and (169) in (164) to obtain

$$-i\hbar \frac{\gamma}{2} = \sum_\lambda \frac{|\langle H' \rangle|^2}{\hbar} \; \frac{1 - \exp[i(\omega_0 - \omega_\lambda)t + \gamma t/2]}{(\omega_0 - \omega_\lambda) - i(\gamma/2)} \tag{170}$$

where $\langle H' \rangle \equiv \langle a\lambda \mid H' \mid 1 \rangle$. The summaticn on the right hand side of the above equation is over a number of states λ with very nearly the same frequency. Under these circumstances, the summation can be replaced by an integral

$$\sum_\lambda \rightarrow \iint N(\omega)\, d\omega\, d\Omega \tag{171}$$

where $N(\omega)$ represents the density of states (see Eq. 107). Equation (170) then becomes

$$\gamma = \frac{2i}{\hbar}\left[\frac{1}{\hbar}\iint |\langle H' \rangle|^2 N(\omega)\, J(\omega)\, d\omega\, d\Omega\right] \tag{172}$$

where

$$J(\omega) = \frac{1 - \exp[i(\omega_0 - \omega)t]\, e^{\gamma t/2}}{(\omega_0 - \omega) - i(\gamma/2)} \tag{173}$$

We will assume that $\gamma \ll \omega_0$; i.e., the inverse of the lifetime ($\lesssim 10^9$ sec^{-1}) is much smaller than the characteristic frequencies ($\sim 10^{15}$ sec^{-1}), this will indeed follow from the final result. Under this assumption γ can be neglected in Eq. (173) to obtain

$$\begin{aligned} J &\simeq \frac{1 - \exp[i(\omega_0 - \omega)t]}{\omega_0 - \omega} \\ &\simeq \frac{1 - \cos[(\omega_0 - \omega)t]}{(\omega_0 - \omega)} - i\,\frac{\sin[(\omega_0 - \omega)t]}{(\omega_0 - \omega)} \end{aligned} \tag{174}$$

The first term has very rapid variation around $\omega \simeq \omega_0$ and gives negligible contribution to any integral over ω except around $\omega \simeq \omega_0$ where the function itself vanishes. Thus this term will lead to a small imaginary value of γ. We are in any case interested in the real part of γ (which would give the life-time, etc.) which will be given by

$$\gamma \simeq \frac{2}{\hbar}\left[\frac{1}{\hbar}\int |\langle H' \rangle|^2 N(\omega_0)\, d\Omega \int_{-\infty}^{\infty} \frac{\sin(\omega_0 - \omega)t}{(\omega_0 - \omega)}\, d\omega\right] \tag{175}$$

We have made two approximations here. First, we have pulled out factors which are essentially constant in the neighbourhood of $\omega \approx \omega_0$. Secondly, the limits of the integral have been taken from $-\infty$ to $+\infty$ since in any case the contribution vanishes except around ω_0. Thus

$$\gamma \simeq \frac{2\pi}{\hbar}\left[\frac{1}{\hbar}\int |\langle H'\rangle|^2 N(\omega_0)\, d\Omega\ \right]$$

$$= \frac{2\pi}{\hbar}\ \frac{1}{\hbar}\ \frac{V\omega_0^2}{8\pi^3 c^3}\int |\langle H'\rangle|^2\, d\Omega \tag{176}$$

Now

$$H' = \langle a\lambda \,|\, H' \,|\, 1\rangle$$

$$= \langle a; 0, 0, \ldots 1_\lambda, 0 \ldots |\, (-ie) \sum_\lambda \left(\frac{\hbar\omega_\lambda}{2\epsilon_0 V}\right)^{\frac{1}{2}}$$

$$\times\ [a_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} - \bar{a}_\lambda e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}]\, \hat{\mathbf{e}}_\lambda \cdot \mathbf{r} \,|\, b; 0, 0, \ldots 0_\lambda \ldots\rangle$$

$$= (+ie)\left(\frac{\hbar\omega_\lambda}{2\epsilon_0 V}\right)^{\frac{1}{2}} \langle a \,|\, e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\, \mathbf{r} \,|\, b\rangle \cdot \hat{e}_\lambda$$

$$\simeq ie\left(\frac{\hbar\omega_\lambda}{2\epsilon_0 V}\right)^{\frac{1}{2}} \langle a \,|\, \mathbf{r} \,|\, b\rangle \cdot \hat{e}_\lambda \tag{177}$$

where in the last step we have used the dipole approximation (see the discussion after Eq. 97). On substitution in Eq. (176), we get

$$\gamma \simeq \frac{1}{2\pi}\left[\frac{e^2}{4\pi\epsilon_0\, \hbar c}\right]\frac{\omega_0^3}{c^2}\int |\hat{\mathbf{e}}_\lambda \cdot \langle a \,|\, \mathbf{r} \,|\, b\rangle|^2\, d\Omega \tag{178}$$

(cf. Eq. 110). On carrying out the integration and summing over the two states of polarization we get (see Eq. 111),

$$\gamma = A$$

i.e., γ is simply the Einstein A coefficient corresponding to spontaneous emissions as it indeed should be!

Now the probability of a photon being emitted in the mode λ is given by (see Eq. 169)

$$|C_{a\lambda}(t=\infty)|^2 = \frac{|\langle H'\rangle|^2}{\hbar^2}\ \frac{1}{(\omega_0-\omega_\lambda)^2 + \gamma^2/4} \tag{180}$$

If we multiply the above equation by $N(\omega)\, d\omega\, d\Omega$ which gives the number of modes in the frequency ω to $\omega + d\omega$ and in the solid angle $d\Omega$ and carry out the integration over $d\Omega$ and sum over the two states of polarization, we would get

$$g(\omega)\, d\omega = \frac{\gamma}{2\pi}\ \frac{d\omega}{(\omega_0-\omega)^2 + \gamma^2/4} \tag{181}$$

where we have used Eq. (178). The above equation indeed gives us the probability that the spontaneously emitted photon has its frequency between ω and $\omega + d\omega$, which is nothing but the Lorenzian line shape. Notice that the above expression is normalized, which implies that the probability that the atom makes a spontaneous transition from the upper state to the lower state is unity (as $t \rightarrow \infty$) as it indeed should be.

SOLUTION 22.6

$$\langle \alpha \mid N_{op} \mid \alpha \rangle = e^{-|\alpha|^2} \sum_m \frac{\alpha^{*m}}{\sqrt{m!}} \langle m \mid \sum_n \frac{\alpha^n}{\sqrt{n!}}\, n \mid n \rangle$$

(because $N_{op} \mid n \rangle = n \mid n \rangle$; see Problem 8.9)

$$= e^{-|\alpha|^2} \sum_n \frac{|\alpha|^{2n}\, n}{n!} = Ne^{-N} \sum_{n=1,\ldots} \frac{N^{n-1}}{(n-1)!} = N \quad (182)$$

Similarly

$$\langle \alpha \mid N_{op}^2 \mid \alpha \rangle = e^{-N} \sum_n \frac{N^n\, n^2}{n!} = Ne^{-N} \sum \frac{N^{n-1}\,(n-1+1)}{(n-1)!}$$
$$= N^2 + N \quad (183)$$

from which Eq. (148) follows.

SOLUTION 22.8

The differential cross-section $d\sigma$ is given by (see Sec. 20.3):

$$cn\,d\sigma = W d\Omega \quad (184)$$

where $Wd\Omega$ represents the probability (per unit time) of scattering into the solid angle $d\Omega$ and n is the number of photons per unit volume corresponding to one photon in a box of volume, V, i.e.,

$$n = \frac{1}{V} \quad (185)$$

Further, $Wd\Omega$ is given by the Golden rule (see Eq. 38 of Chapter 20):

$$W d\Omega = \frac{2\pi}{\hbar} N(E)\, d\Omega \mid \langle f \mid H' \mid i \rangle \mid^2 \quad (186)$$

where $N(E)$ represents the density of states and for the neutron-proton system in a final state of relative momentum $\mathbf{p}$, it is given by (see Appendix M).

$$N(E)\, d\Omega = \frac{\mu V}{(2\pi\hbar)^3}\, p\, d\Omega, \quad (137)$$

This $N(E)\, d\Omega$ represents the number of states (per unit energy interval) such that the direction of $\mathbf{p}$ lies within a solid angle $d\Omega$ and $\mu = M/2$ is the reduced mass of the $n - p$ system. The kets $\mid i \rangle$ and $\mid f \rangle$ represent the initial and final states and since the initial state contains one photon and the final state none, we have (cf. Eq. 97)

$$\langle f \mid H' \mid i \rangle \simeq \frac{q}{m}\left(\frac{\hbar}{2\epsilon_0 V\omega}\right)^{1/2} \hat{\mathbf{e}} \cdot \langle a \mid \mathbf{p} \mid b \rangle \tag{188}$$

where M is the proton mass. Thus

$$d\sigma = \frac{V\alpha}{4\pi\hbar^2\omega M} p \mid \hat{\mathbf{e}} \cdot \langle a \mid \mathbf{p} \mid b \rangle \mid^2 d\Omega \tag{189}$$

where

$$\alpha = \frac{q^2}{4\pi\epsilon_0 \hbar c} \simeq \frac{1}{137}$$

is the fine structure constant and we have used the fact that $\mu = M/2$. Integration over all directions gives a factor $4\pi/3$. Thus

$$\sigma = \frac{1}{3} \alpha \frac{pV}{\hbar^2 \omega M} \mid \langle a \mid \mathbf{p} \mid b \rangle \mid^2 \tag{190}$$

The two states are given by

$$\mid b \rangle = \sqrt{\frac{K}{2\pi}} \frac{e^{-Kr}}{r} \tag{191}$$

$$\mid a \rangle = \frac{1}{\sqrt{V}} \exp[i\,\mathbf{p} \cdot \mathbf{r}/\hbar] \tag{192}$$

The final state corresponds to a free neutron proton system. We must remember that in Eq. (190), $\mathbf{p}$ is the operator $-i\hbar\nabla$. The integration, however, poses no problem because*

$$\begin{aligned} \mid \langle a \mid \mathbf{p} \mid b \rangle \mid^2 &= \mid \langle b \mid \mathbf{p} \mid a \rangle \mid^2 \\ &= \mathbf{p}^2 \mid \langle b \mid a \rangle \mid^2 \\ &= p^2 \frac{K}{2\pi V} \left| \int \frac{e^{-Kr}}{r} \exp[i\,\mathbf{p} \cdot \mathbf{r}/\hbar]\, r^2\, dr \sin\theta\, d\theta\, d\varphi \right|^2 \\ &= \frac{Kp^2}{2\pi V} (2\pi)^2 \left| \int_0^\infty \int_0^\pi e^{-Kr} \exp[ipr \cos\theta/\hbar]\, r dr \sin\theta\, d\theta \right|^2 \end{aligned}$$

where we have chosen the polar axis along $\mathbf{p}$. Carrying out the integrations we get

$$\sigma = \frac{8\pi}{3} \frac{\alpha}{M\hbar^2\omega} \frac{p^3 K}{(p^2/\hbar^2 + K^2)^2} \tag{193}$$

---

*Notice that the final state is an eigenstate of $\mathbf{p}$, i.e.,

$$\mathbf{p} \exp(i\mathbf{p} \cdot \mathbf{r}/\hbar) = -i\hbar\nabla \exp(i\mathbf{p} \cdot \mathbf{r}/\hbar) = \mathbf{p} \exp[i\mathbf{p} \cdot \mathbf{r}/\hbar]$$

where on the right hand side, $\mathbf{p}$ is simply a number.

If B is the binding energy of the deuteron, then

$$\hbar\omega - B = p^2/M \tag{194}$$

(This relation is slightly incorrect since the incident quantum carries a momentum $\hbar\omega/c$ which will give the centre of mass some energy as well). Also it can be shown that the binding energy is related to the parameter K though the equation $\hbar K = (MB)^{1/2}$. We have finally

$$\sigma \simeq \frac{8\pi}{3}\,\alpha\,\frac{\hbar^2}{M}\,\frac{B^{1/2}\,(\hbar\omega - B)^{3/2}}{(\hbar\omega)^3} \tag{195}$$

The above equation gives the cross-section for photodisintegration of deuteron corresponding to the electric dipole moment interaction and is in good agreement with the expêrimental data at high γ-ray energies (see, e.g., Bethe and Morrison, 1956 for a good discussion on comparison with experimental data).

SOLUTION 22.9

(*a*)
$$\begin{aligned}
\sum_s (E_s - E_n)\,|\langle s \,|\, x \,|\, n\rangle|^2 &= \sum_s (E_s - E_n)\,\langle n \,|\, x \,|\, s\rangle\,\langle s \,|\, x \,|\, n\rangle \\
&= \sum_s \langle n \,|\, xH_0 - H_0\,x \,|\, s\rangle\,\langle s \,|\, x \,|\, n\rangle \text{ (see Eqs. 15 and 16)} \\
&= \frac{i\hbar}{m}\sum_s \langle n \,|\, p_x \,|\, \rangle s\,\langle s \,|\, x \,|\, n\rangle \text{ (using Eq. 17)} \\
&= \frac{i\hbar}{m}\,\langle n \,|\, p_x\,x \,|\, n\rangle \text{ (because } \sum_s |\, s\rangle\,\langle s \,| = 1) \qquad (196)
\end{aligned}$$

We could also write

$$\begin{aligned}
\sum_s (E_s - E_n)\,|\langle s \,|\, x \,|\, n\rangle|^2 &= \sum \langle n \,|\, x \,|\, s\rangle\,\langle s \,|\, H_0x - xH_0 \,|\, n\rangle \\
&= -\frac{i\hbar}{m}\,\langle n \,|\, xp_x \,|\, n\rangle \qquad (197)
\end{aligned}$$

Thus

$$\begin{aligned}
\sum_s \langle E_s - E_n)\,|\langle s \,|\, x \,|\, n\rangle|^2 &= -\frac{i\hbar}{2m}\,\langle n \,|\, xp_x - p_x x \,|\, n\rangle \\
&= \hbar^2/2m
\end{aligned}$$

This can be generalized to more than one electron in which case we get

$$\sum_i \sum_s (E_s - E_n)\,|\langle s \,|\, x_i \,|\, n\rangle|^2 = \frac{\hbar^2}{2m}\,Z \tag{198}$$

where Z is the atomic number. Equation (198) is referred as the dipole sum rule or sometimes also as the Thomas-Reiche-Kuhn sum role. The factors

$$\frac{2m}{\hbar^2}(E_s - E_n)\,|\langle s \,|\, x \,|\, n\rangle|^2 = f_{sn} \tag{199}$$

are called oscillator strengths. The reason for this terminology is that classically, f_{sn} gives the number of electrons moving with oscillator frequency ω_{sn}. The quantum mechanical result, Eq. (199), shows that they need not be integers.

(*b*) We start with the formula for the cross-section in the dipole approximation (see Eqs. 184-186)

$$\frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar}\,\frac{N(E)}{c/V}\,|\langle f \,|\, H' \,|\, i\rangle|^2 \tag{200}$$

$$= 4\pi^2\alpha\,(E_s - E_n)\,|\,\hat{e}\cdot\langle s \,|\, \mathbf{r} \,|\, n\rangle|^2 N(E) \text{ (Using Eq. 28)} \tag{201}$$

If we integrate this over dE, the right hand side of Eq. (201) may be regarded as sum over final states to give

$$\int \sigma\, dE = 4\pi^2\alpha \sum_s (E_s - E_n)\,|\langle s \,|\, \hat{e}\cdot\mathbf{r} \,|\, n\rangle|^2 \tag{202}$$

We consider a beam of photons with a fixed linear polarization, say $\hat{e}$ along the x-direction. We then have

$$\int \sigma\, dE = 4\pi^2\alpha \sum_s (E_s - E_n)\,|\langle s \,|\, x \,|\, n\rangle|^2$$

$$= \frac{2\pi^2\alpha\hbar^2}{m} \tag{203}$$

SOLUTION 22.10

For the electron initially in the K shell (ejection from which is comparitively probable), the initial wavefunction is given by

$$\psi_i = \left(\frac{1}{\pi a^3}\right)^{\frac{1}{2}} e^{-r/a} \tag{204}$$

where

$$a = \frac{a_0}{Z} = \frac{\hbar^2}{m}\left(\frac{4\pi\epsilon_0}{q^2}\right)\frac{1}{Z} = \frac{\hbar^2}{me^2}\,\frac{1}{Z} \tag{205}$$

For the evaluation of the matrix element the assumption will be made that $\hbar\omega$ is much larger than the ionization potential of the atom so that to a good approximation, the final state can be represented by

$$\psi_f = \frac{1}{\sqrt{V}}\, e^{i\mathbf{k}_1\cdot\mathbf{r}} \tag{206}$$

where $\mathbf{k}_1$ represents the electron wave vector; we have put a subscript to $\mathbf{k}$ so that there is no confusion with the wave vector associated with the electromagnetic wave (see Eq. 208). Now the perturbing potential may be taken as (see Eq. 7)

$$H' = \frac{q}{m}\,\mathbf{A}\cdot\mathbf{p} \tag{207}$$

where

$$\mathbf{A} = \hat{\mathbf{e}}\,A_0 \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)] + cc \tag{208}$$

or

$$\mathbf{A} = 2\,\hat{\mathbf{e}}\,|\,A_0\,|\cos(\mathbf{k}\cdot\mathbf{r} - \omega t + \phi) \tag{209}$$

In Eq. (208) '*cc*' denotes the complex conjugate of the first term so that A is necessarily real. Now, according to first order perturbation theory, the amplitude of the final state at time t is given by (see Eq. 14 of Chapter 20)

$$\begin{aligned} C_f(t) &= \frac{1}{i\hbar}\int_0^t H'_{fi}(t)\exp[i\omega_{fi}t]\,dt \\ &= \frac{M_1}{i\hbar}\,\frac{\exp[i(\omega_{fi}-\omega)t]-1}{(\omega_{fi}-\omega)} + \frac{M_2}{i\hbar}\,\frac{\exp[i(\omega_{fi}+\omega)t]-1}{(\omega_{fi}+\omega)} \end{aligned} \tag{210}$$

where

$$M_1 = -\frac{iqA_0}{m}\,\hat{\mathbf{e}}\cdot\int \psi_f^*\,e^{i\mathbf{k}\cdot\mathbf{r}}\,\mathbf{p}\psi_i\,d\tau$$

and

$$M_2 = -\frac{iqA_0^*}{m}\,\hat{\mathbf{e}}\cdot\int \psi_f^*\,e^{-i\mathbf{k}\cdot\mathbf{r}}\,\mathbf{p}\,\psi_i\,d\tau$$

As discussed in Sec. 20.3, the first term on the RHS of Eq. (210) contributes in an absorption process and the second term contributes in an emission process. Since we are interested in an absorption of a photon, we have [cf. Eq. (16) of Chapter 20]

$$P_f(t) = |\,C_f(t)\,|^2 = |\,M_1\,|^2\,\frac{1}{\hbar^2}\left[\frac{\sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)/2}\right]^2 \tag{211}$$

Following a procedure similar to that discussed in Sec. 19.2, we get the following expression for the transition probability to solid angle $d\Omega$

$$W d\Omega = \frac{2\pi}{\hbar}\,|\,M_1\,|^2\,N(E)\,d\Omega \tag{212}$$

where

$$N(E)\,d\Omega = \frac{mk_1 V}{8\pi^3\hbar^2}\,d\Omega \tag{213}$$

represents the density of final states (see Appendix M). Thus

$$W d\Omega = \frac{2\pi}{\hbar} \cdot \frac{m k_1 V}{8\pi^3 \hbar^2} \cdot |M_1|^2 d\Omega \tag{214}$$

Now, the electric field associated with the electromagnetic wave is given by

$$\mathcal{E} = -\frac{\partial \mathbf{A}}{\partial t} = -2\omega\,|A_0|\,\hat{\mathbf{e}} \sin(\mathbf{k}\cdot\mathbf{r} - \omega t + \varphi)$$

The time averaged energy density is given by (see Eq. 46)

$$\epsilon_0 4\omega^2\,|A_0|^2 \cdot \tfrac{1}{2}$$

Thus

$$\text{Incident Intensity} = 2\epsilon_0\omega^2 c\,|A_0|^2$$

and

$$\text{Incident Flux} = \frac{\text{Incident Intensity}}{\hbar\omega} = \frac{2\epsilon_0\,\omega c}{\hbar}\,|A_0|^2 \tag{215}$$

Hence

$$d\sigma = \frac{W d\Omega}{\text{Incident Flux}}$$

or

$$\frac{d\sigma}{d\Omega} = \frac{m k_1 V}{8\pi^2\hbar^3\,\epsilon_0\omega\, c\,|A_0|^2}\,|M_1|^2 \tag{216}$$

Now

$$M_1 = -\frac{iq}{m} A_0 \frac{1}{V^{1/2}}\,\hat{\mathbf{e}} \cdot \int e^{-i\mathbf{k}_1\cdot\mathbf{r}}\, e^{i\mathbf{k}\cdot\mathbf{r}}\,\mathbf{p}\psi_i d\tau$$

But

$$\int \phi\, p_x \psi\, d\tau = -i\hbar \int \phi \frac{\partial\psi}{\partial x}\, d\tau = i\hbar \int \psi \frac{\partial\phi}{\partial x}\, d\tau$$
$$= -\int \psi p_x\, \phi d\tau$$

Thus

$$\int \phi \mathbf{p}\, \psi\, d\tau = -\int \psi \mathbf{p}\, \phi\, d\tau = +i\hbar \int \psi \nabla \phi\, d\tau \tag{217}$$

This also follows from the Hermitian property of **p** (see Problem 8.14), Using

Eq. (217) we get

$$M_1 = \frac{q\hbar}{m} A_0 \frac{1}{V^{1/2}} \hat{\mathbf{e}} \cdot \int \psi_i \nabla \exp\,[i(\mathbf{k}_1 - \mathbf{k}) \cdot \mathbf{r}]\, d\tau$$

$$= -\frac{iq\hbar A_0}{m}\left(\hat{\mathbf{e}} \cdot \mathbf{k}_1\right)\frac{1}{V^{1/2}}\int\left[\frac{1}{\pi a^3}\right]^{\frac{1}{2}} \exp\left[-i\mathbf{K} \cdot \mathbf{r} - \frac{r}{a}\right] d\tau \tag{218}$$

where we have used the transverse character of light waves (i.e., $\hat{\mathbf{e}} \cdot \mathbf{k} = 0$) and

$$\mathbf{K} = \mathbf{k}_1 - \mathbf{k} \tag{219}$$

is the momentum transfer in units of $\hbar$. In carrying out the integration, we choose the polar axis along $\mathbf{K}$ to obtain an expression for $|M_1|^2$ which on substitution in Eq. (216) gives

$$\frac{d\sigma}{d\Omega} = \frac{32\alpha\, \hbar k_1}{m\omega}\left(\hat{\mathbf{e}} \cdot \mathbf{k}_1\right)^2\left(\frac{Z}{a_0}\right)^5\left[\left(\frac{Z}{a_0}\right)^2 + K^2\right]^{-6} \tag{220}$$

where α is the fine structure constant. The above expression is in agreement with the experimental data. For a more thorough treatment of the photoelectric effect, see Heitler (1954) Sec. 21.

CHAPTER TWENTY-THREE

Relativistic Theory

23.1 Introduction

The quantum theory developed so far is non-relativistic. That it is not invariant under Lorentz transformations is obvious if one notes that the time-dependent Schrödinger equation contains the first derivative in time and second derivatives in space coordinates. A simple procedure for building a relativistic theory is to follow an approach analogous to the one followed for the non-relativistic theory which is to start with the Hamiltonian formulation, with a relativistically correct Hamiltonian, and to replace the classical observables by operators. This is essentially the procedure we adopt in this chapter. But it must be pointed out that the success of the procedure is limited because it soon turns out that such a theory is logically deficient. For one thing, it turns out that one cannot, even in principle, imagine a system in which there is only one particle since the law of conservation of particles is itself not necessarily true. Nevertheless, the ideas presented here are the basic framework for building up satisfactory relativistic theories.

From the point of view of specific predictions, the non-relativistic theory fails in some major features. It fails to explain the spin of an elementary system, such as the electron, and the consequences thereof. Moreover, the theory cannot give a satisfactory account of high energy phenomena such as pair production, bremmstrahlung, etc.

23.2 The Klein-Gordon Equation

We start with the relativistic Hamiltonian for a free particle

$$H = \sqrt{c^2p^2 + m^2c^4} \tag{1}$$

where p is the momentum, m the rest mass.

Introducing the operators $E \to i\hbar\, \partial/\partial t$

$$\mathbf{p} \to \frac{\hbar}{i} \nabla \text{ and writing } H\psi = E\psi$$

we obtain

$$[-c^2\hbar^2\nabla^2 + m^2c^4]^{1/2}\, \psi = i\hbar\, \frac{\partial\psi}{\partial t}$$

an equation beyond which theory can proceed only if we have a consistent scheme for interpreting the square root of the above operator. This *can* be done but leads to difficulties.* We avoid them by squaring the relation (1) and replacing by the operators to obtain

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*See Baym (1969).

$$(-c^2\hbar^2\nabla^2 + m^2c^4)\,\psi = -\hbar^2\,\frac{\partial^2\psi}{\partial t^2}$$

Dividing by $c^2\hbar^2$ and rearranging the terms, we obtain the Klein-Gordon equation

$$\left(\Box - \frac{m^2c^2}{\hbar^2}\right)\psi = 0 \tag{2}$$

where we have introduced the d'Alembertian operator

$$\Box = \nabla^2 - \frac{1}{c^2}\,\frac{\partial^2}{dt^2}$$

The Klein-Gordon equation, it turns out, is the correct one for spinless particles and not for electrons. Although this equation is an important one for further developments of relativistic field theories, we shall not discuss it further here. The reason is that the equation is valid for certain classes of particles such as the π- and K-mesons which are strongly interacting. The approximation methods of elementary quantum mechanics, such as the perturbation theory, are usually inadequate for these anyway.

23.3. The Dirac Equation

The original argument of Dirac, in search of a relativistic equation was that it must be a first-order differential equation in time because knowledge of the wavefunction alone at an initial time t_0 should suffice to predict its value at a later time. Since, in relativity, time and space coordinates are treated symmetrically, the equation (he argued) must be a first-order differential equation in space coordinates as well. Dirac started with a Hamiltonian of the form

$$H = c\,(\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z) + \beta mc^2 \tag{3}$$

where the coefficients α_1, α_2, α_3 and β are not mere numbers but (square) matrices. For brevity, we shall often write (3) as $H = c\,\alpha\cdot\mathbf{p} + \beta mc^2$; it must be clear that α is *not* to be thought of as a vector. The wave equation corresponding to this Hamiltonian is

$$i\hbar\,\frac{\partial\psi}{\partial t} = \frac{c\hbar}{i}\,(\alpha\cdot\nabla\psi) + \beta mc^2\psi \tag{4}$$

Since α and β are allowed to be matrices of numbers, it follows that the wavefunction ψ must have more than one component; i.e., at each point the state of the particle will be described by more than one wavefunction. It follows that Eq. (4) will be capable of describing a particle with additional intrinsic degrees of freedom.

The Hamiltonian (3) must still satisfy the energy-momentum relation

$$E^2 = H^2 = c^2p^2 + m^2c^4 \tag{5}$$

We introduce the notation $p_1 = p_x$, $p_2 = p_y$, $p_3 = p_z$, $p_4 = iE/c$; $x_1 = x$, $x_2 = y$, $x_3 = z$ and $x_4 = +ict$. Equation (3) becomes

$$H = c\sum_{j=1}^{3} \alpha_j p_j + \beta mc^2$$

and

$$H^2 = c^2\left\{\sum_{j}\sum_{\substack{k\\ j\neq k}} (\alpha_j\alpha_k + \alpha_k\alpha_j)\, p_j p_k + \sum_{j=1}^{3} \alpha_j^2 p_j^2 + mc^3\sum_{j=1}^{3} (\alpha_j\beta + \beta\alpha_j)\, p_j + m^2c^4\beta^2\right\} \tag{6}$$

Eqs. (5) and (6) are consistent if

$$\left.\begin{aligned} \alpha_j\alpha_k + \alpha_k\alpha_j &= 0 \qquad (\text{for}\, j \neq k)\\ \alpha_j\beta + \beta\alpha_j &= 0\\ \alpha_j^2 = 1,\ \alpha_k^2 &= 1 \end{aligned}\right\} \tag{7}$$

Since Eqs. (7) are to be matrix relations, the symbols 0 and 1 on the right ought to be regarded as the null matrix and the unit matrix respectively.

We first show that these matrices must be of even dimension. We have, for example,

$$\alpha_1\beta = -\beta\alpha_1$$

Multiplying by α_1 on the left, setting $\alpha_1^2 = 1$ and taking the trace, we obtain

$$\begin{aligned} \text{Trace}\,\beta = -\,\text{Trace}\,(\alpha_1\beta\alpha_1) &= -\,\text{Trace}\,(\alpha_1^2\beta)\\ &= -\,\text{Trace}\,\beta \end{aligned}$$

We have used the result Trace (ABC) = Trace (CAB). We therefore have Trace $\beta = 0$, a result which applies to each of the α matrices as well. Eqs. (7) also tell us that the eigenvalues of the matrices must be ± 1. Since the trace is just the sum of all the eigenvalues, it follows that the $+1$ and -1 eigenvalues must occur the same number of times. Hence each of the matrices must be of even dimension N. Now N cannot be 2, since we can only have three 2×2 independent non-commuting matrices. We shall see that 4×4 matrices satisfy all the conditions.

There is seldom any need for a specific representation of these matrices

Nevertheless, for fixing our ideas, we shall choose the following representation.

$$\alpha_1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \qquad \alpha_2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}$$

$$\alpha_3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{8}$$

We note that all these matrices are Hermitian, i.e.,

$$\alpha^\dagger = \alpha, \qquad \beta^\dagger = \beta$$

We can shorten these by introducing the Pauli matrices.

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \quad \text{or} \quad \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}$$

and

$$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{9}$$

Each element in (9) is itself a 2 × 2 matrix.*

Eq. (4) can be written as

$$-\frac{\partial\psi}{\partial x_4} = \frac{1}{i}\,\alpha\cdot\nabla\psi + \beta\frac{mc}{\hbar}\,\psi$$

Multiplying by β on the left side, we have

$$-i\beta\alpha\cdot\nabla\psi + \beta\,\frac{\partial\psi}{\partial x_4} + \frac{mc}{\hbar}\,\psi = 0$$

We define the following four γ matrices.

$$\gamma = -i\beta\alpha \text{ (i.e., } \gamma_j = -i\beta\alpha_j)$$
$$\gamma_4 = \beta$$

Note that *these* γ matrices are also Hermitian, i.e., $\gamma_\mu{}^\dagger = \gamma_\mu$. The Dirac equation now takes the form

$$\left(\sum_{\mu=1}^{4} \gamma_\mu \frac{\partial}{\partial x_\mu}\,\psi + \kappa\right)\psi = 0$$

---

*Eqs. (9) are not just a mnemonic. One can use them in algebra; for example

$$\alpha_1\beta = \begin{pmatrix} 0 & \sigma_1 \\ \sigma_1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 0 & -\sigma_1 \\ \sigma_1 & 0 \end{pmatrix}$$

It is easily checked that the result of starting with 4 × 4 matrices is identical.

where $\varkappa = mc/\hbar$. It is usual to drop the summation over the repeated index μ and write simply

$$\left(\gamma_\mu \frac{\partial\psi}{\partial x_\mu} + \varkappa\right)\psi = 0 \tag{10}$$

(A convention we shall adopt is to use Greek indices λ, μ, ν, etc., when their values range from 1 to 4 and Roman ones i, j, k, etc., for values ranging from 1 to 3). In terms of the momentum operator, we can write

$$(\gamma_\mu p_\mu - imc)\,\psi = 0 \tag{11}$$

Finally, introducing the Feynman notation

$\gamma_\mu a_\mu = \not{a}$ etc., we can also write the Dirac equation in the forms

$$\text{or} \qquad (\not{p} - im_0 c)\,\psi = 0 \tag{12}$$

$$(\not{\nabla} + \varkappa)\,\psi = 0$$

Eqs. (10), (11) and (12) are the covariant forms of Dirac equation; they do not appear to single out the space and time parts. However, writing them in those forms does not automatically guarantee that the equation is covariant under Lorentz transformations.*

23.4. Probability and Current Densities

We introduce the Hermitian conjugate (adjoint) matrix $\psi^\dagger = (\psi_1^* \; \psi_2^* \; \psi_3^* \; \psi_4^*)$ which is a 1-row 4-column matrix. Multiplying Eq. (4) on the left by $\psi^\dagger$, we have

$$i\hbar\psi^\dagger \frac{\partial\psi}{\partial t} = \frac{c\hbar}{i}\psi^\dagger\alpha\cdot\nabla\psi + mc^2\psi^\dagger\beta\psi \tag{13}$$

Similarly, starting with the adjoint of Eq. (4),

$$-i\hbar\frac{\partial\psi^\dagger}{\partial t} = -\frac{c\hbar}{i}\nabla\psi^\dagger\cdot\alpha + mc^2\psi^\dagger\beta$$

---

*It is clear that these equations are meaningful only if we interpret ψ as a 4 row, 1 column matrix (i.e., a spinor with 4 components). Eq. (10) is a shorthand for the four equations ($\lambda = 1, 2, 3, 4$)

$$\sum_{\mu=1}^{4}\sum_{\sigma=1}^{4}\{(\gamma_\mu)_{\lambda\sigma}p_\mu - imc\,\delta_{\lambda\sigma}\}\,\psi_\sigma = 0$$

where $(\gamma_\mu)_{\lambda\sigma}$ is the $\lambda\sigma$th component of the matrix γ_μ and $\delta_{\lambda\sigma}$ the $\lambda\sigma$th component of the unit matrix. The summation over μ runs over 4 terms because there are 4 space-time components. On the other hand, λ and σ take values 1 to 4 because the Dirac matrices happen to be 4-dimensional. This, if one is not alert, causes some confusion in algebraic work. It is never really necessary to write the equation in this elaborate form, but if ever in doubt the reader is advised to write it out in full.

(recall that α, β are Hermitian) and after multiplying by ψ, we obtain

$$-i\hbar\left(\frac{\partial\psi^\dagger}{\partial t}\right)\psi = -\frac{c\hbar}{i}\nabla\psi^\dagger\cdot\alpha\psi + mc^2\psi^\dagger\beta\psi \tag{14}$$

Subtracting (14) from (13), we can obtain the following,

$$\frac{\partial}{\partial t}(\psi^\dagger\psi) + c\nabla\cdot(\psi^\dagger\alpha\psi) = 0 \tag{15}$$

This equation is the continuity equation

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{j} = 0$$

provided we make the identification

$$\rho = \psi^\dagger\psi = \sum_{\lambda=1}^{4}\psi_\lambda^*\psi_\lambda$$

and

$$\mathbf{j} = c\psi^\dagger\alpha\psi = c\sum_{\lambda,\sigma=1}^{4}\psi_\lambda^*(\alpha)_{\lambda\sigma}\psi_\sigma \tag{16}$$

In Eq. (16) our notation of writing $\mathbf{j}$ as a vector anticipates a result, namely, that $\psi^\dagger\alpha\psi$ transforms as a vector. One can express the quantities ρ and $\mathbf{j}$ in compact form, writing

$$\psi = \bar{\psi}^\dagger\gamma_4 \quad\text{and}\quad \psi^\dagger = \bar{\psi}\gamma_4$$

so that

$$\rho = \psi^\dagger\psi = \bar{\psi}\gamma_4\psi$$

and

$$\mathbf{j} = c\psi^\dagger\alpha\psi = c\bar{\psi}\gamma_4\alpha\psi = ic\bar{\psi}\gamma\psi$$

Thus, if we write

$$j_x = j_1 \text{ etc.} \quad\text{and}\quad j_4 = ic\rho$$

we have

$$j_\mu = ic\bar{\psi}\gamma_\mu\psi$$

The continuity equation is

$$\frac{\partial j_\mu}{\partial x_\mu} = 0 \tag{18}$$

23.5. Covariance of Dirac Equation

Let us first see what covariance demands. Assume that there are two observers in Lorentz frames Σ and Σ'. We require that scalar quantities remain the same in the two systems while four vectors must transform like the space-time coordinates. Finally, although the wavefunctions for the two observers need not be the same, the recipe for writing down Dirac equation must be the same for both observers. The equation in Σ and Σ' are to be

$$\left(\gamma_\mu \frac{\partial}{\partial x_\mu} + \kappa\right)\psi(x_\mu) = 0$$

$$\left(\gamma_\mu \frac{\partial}{\partial x'_\mu} + \kappa\right)\psi'(x'_\mu) = 0 \tag{19}$$

Notice that the γ_μ are the same in both frames; they define the recipe and ought not to be changed.* The coordinates x and x' are related through

$$x'_\nu = a_{\nu\mu} x_\mu \tag{20a}$$

and the inverse transformations

$$x_\mu = a_{\nu\mu} x'_\nu \tag{20b}$$

with the restrictions

$$a_{\lambda\mu} a_{\mu\nu} = \delta_{\lambda\nu} \tag{20c}$$

We have

$$\frac{\partial\psi}{\partial x_\mu} = \frac{\partial\psi}{\partial x'_\nu}\frac{\partial x'_\nu}{\partial x_\mu} = a_{\nu\mu}\frac{\partial\psi}{\partial x'_\nu}$$

Writing

$$\psi'(x'_\mu) = S\,\psi(x_\mu)$$

and the inverse relation

$$\psi(x_\nu) = S^{-1}\psi'(x'_\nu) \tag{21}$$

we can rewrite the first of Eqs. (19) as

$$\left(\gamma_\mu a_{\nu\mu} \frac{\partial}{\partial x'_\nu} + \kappa\right) S^{-1}\psi'(x'_\mu) = 0$$

Multiplying on the left by S, we have

$$\left(a_{\nu\mu}\, S\gamma_\mu S^{-1} \frac{\partial}{\partial x'_\nu} + \kappa\right)\psi'(x'_\mu) = 0 \tag{22}$$

---

*It turns out that a different set γ'_μ related to γ_μ by a unitary transformation can be defined giving entirely equivalent results. We prefer to start with the same γ in order to emphasize the physical principle of covariance.

This is identical with the second of Eqs. (19) provided we can find an S which satisfies

$$a_{\nu\mu}\, S\gamma_\mu\, S^{-1} = \gamma_\nu$$

Multiplying by $a_{\lambda\nu}$, summing over ν and using relation (20c), we obtain

$$S\gamma_\lambda\, S^{-1} = a_{\lambda\nu}\gamma_\nu \tag{23}$$

For the complete proof of convariance one has to show that such an S exists. Here we merely assert that this is true and refer the interested reader to other works* for explicit construction of S for every type of Lorentz transformation. Eq. (23) suggests that a set of matrices $\gamma'_\lambda = a_{\lambda\nu}\gamma_\nu$ will obey all the commutation properties of γ_ν and would serve just as well. One could, therefore, have written down the equation in Σ' frame as

$$\left(\gamma'_\lambda \; \frac{\partial}{\partial x'_\lambda} + \kappa \right) \psi\; (x'_\lambda) = 0 \tag{24}$$

and γ'_λ and γ_ν are related exactly as four vectors are in the two frames. Nevertheless, one must remember that the four γ_λ are matrices and cannot be regarded as a physical vector.

However, the current $j_\mu = ic\, \bar{\psi}\, \gamma\psi$ can indeed be shown to transform like a four vector.

23.6. Plane Wave Solutions

We shall find it convenient to start with the free particle equation in terms of α and β.

$$(c\alpha \cdot \hat{\mathbf{p}} + \beta mc^2)\, \psi\, (\mathbf{r}, t) = \hat{E}\, (\mathbf{r}, t) \tag{25}$$

where we have explicitly indicated that $\hat{\mathbf{p}}$ and $\hat{E}$ are operators. We try plane wave solutions

$$\psi\, (\mathbf{r}, t) = \chi \exp\left(\frac{i}{\hbar}\; (\mathbf{p} \cdot \mathbf{r} - Et) \right) \tag{26}$$

where $\mathbf{p}$ and E are now numbers, not operators and the χ are spinors. Clearly Eq. (25) is satisfied if χ obeys the equation

$$(c\alpha \cdot \mathbf{p} + \beta mc^2)\, \chi = E\chi \tag{27}$$

Again in (27), $\mathbf{p}$ and E are now numbers.

Since α and β can be conveniently represented in terms of 2×2 matrices, we start by writing

$$\chi = \begin{pmatrix} u \\ v \end{pmatrix}$$

---

*Bjorken and Drell (1964). Also Eisele (1969).

where u, v are themselves 2-component spinors. Using the relations (9), we obtain

$$\left(c \begin{pmatrix} 0 & \sigma \cdot \mathbf{p} \\ \sigma \cdot \mathbf{p} & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} mc^2 \right) \begin{pmatrix} u \\ v \end{pmatrix} = E \begin{pmatrix} u \\ v \end{pmatrix} \tag{28}$$

We can recover the four equations, if we want, by writing

$$u = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}, \quad v = \begin{pmatrix} u_3 \\ u_4 \end{pmatrix}$$

after solving for u and v. Eq. (28) gives

$$c\sigma \cdot \mathbf{p} v = (E - mc^2)\, u \tag{29a}$$

$$c\sigma \cdot \mathbf{p} u = (E + mc^2)\, v \tag{29b}$$

We can decouple u, v by solving (say) for v from (29b) and substituting in (29a). This gives

$$v = \frac{c\sigma \cdot \mathbf{p}}{E + mc^2}\, u$$

and

$$\frac{c^2\, (\sigma \cdot \mathbf{p})\, (\mathbf{p} \cdot \sigma)}{E + mc^2}\, u = (E - mc^2)\, u$$

Since

$$\sigma \cdot \mathbf{p}\; \sigma \cdot \mathbf{p} = p^2 \text{ (a number)},$$

we have

$$c^2p^2u = (E^2 - m^2v^4)\, u$$

Apart from the trivial solution $u = 0$ (and hence $v = 0$) we have the result

$$E = \pm \sqrt{c^2p^2 + m^2c^4} = E_{\pm} \tag{30}$$

We note that for small momenta [see Eqs. (29)]

$$|\, v \,| \sim \frac{cp}{2mc^2}\, |\, u \,| \sim \frac{V}{2c}\, |\, u \,| \quad (\text{for } E = E_{+})$$

and

$$|\, u \,| \sim \frac{V}{2c}\, |\, v \,| \quad (\text{for } E = E_{-})$$

where V is the velocity of the particle. Thus, for positive energies, u are large components and for negative energies the v are large. For $E = E_{+}$, we express v in terms of u

$$v = \frac{c\sigma \cdot \mathbf{p}}{E_{+} + mc^2} \cdot u \tag{31a}$$

Similarly for $E = E_-$, we express u in terms of v

$$u = \frac{c\sigma \cdot \mathbf{p}}{E_- - mc^2}\, v \tag{31b}$$

We can now obtain 4 linearly independent solutions from Eqs. (31) as follows. Writing

$$u = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ or } u = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

and substituting in (31a), in turn, we obtain two solutions. For example, $u = \binom{1}{0}$ gives

$$\begin{aligned} v = \begin{pmatrix} u_3 \\ u_4 \end{pmatrix} &= \left(\frac{c}{E_+ + mc^2}\right)\begin{pmatrix} p_z & p_x - ip_y \\ p_x + ip_y & -p_z \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= \left(\frac{c}{E_+ + mc^2}\right)\begin{pmatrix} p_z \\ p_x + ip_y \end{pmatrix} \end{aligned}$$

This solution is therefore,

$$\chi_{\downarrow}^{+} = N\begin{pmatrix} u \\ v \end{pmatrix} = N\begin{pmatrix} 1 \\ 0 \\ cp_z/(E_+ + mc^2) \\ cp_+/(E_+ + mc^2) \end{pmatrix}$$

The other solution for $E = E_+$ can be constructed in the same way.

$$\chi_{\downarrow}^{+} = N\begin{pmatrix} 0 \\ 1 \\ cp_-/(E + mc^2) \\ -cp_z/(E + mc^2) \end{pmatrix}$$

Similarly, for $E = E_-$, we choose $v = \binom{1}{0}, \binom{0}{1}$ in turn and substitute in (31b) to obtain

$$\chi_{\uparrow}^{-} = N\begin{pmatrix} cp_z/(E_- - mc^2) \\ cp_+/(E_- - mc^2) \\ 1 \\ 0 \end{pmatrix}, \quad \chi_{\downarrow}^{-} = N\begin{pmatrix} cp_-/(E_- - mc^2) \\ -cp_z/(E_- - mc^2) \\ 0 \\ 1 \end{pmatrix} \tag{32}$$

In these equations we have used the symbols

$$p_\pm = p_x \pm ip_y$$

and the normalization N is chosen to satisfy

$$\chi^\dagger \chi = 1$$

for each of the solutions. It is easily shown that

$$N = \left[1 + \frac{c^2p^2}{(|E| + mc^2)^2}\right]^{-\frac{1}{2}} \tag{33}$$

and the different solutions (32) are orthogonal,

$$\chi_a \chi_b = 0$$

The complete plane wave solutions take the form

$$\psi_{p\sigma}(\mathbf{r}, t) = \chi_{p\sigma} \exp\left[\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} - Et)\right] \tag{34}$$

The suffix p is to tell us that we are dealing with plane waves of momentum p and the suffix σ is to identify one of the 4 solutions [(32)].

23.7. Coulomb Scattering: Relativistic Formula

As an example of the use of spinors, we calculate the relativistic correction for the cross-section for Coulomb scattering of an electron by a heavy scatterer. It may be recalled that the non-relativistic scattering amplitude in the Born approximation, is given by

$$f(\theta, \varphi) = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int e^{-i\mathbf{k}'\cdot\mathbf{r}}\, V(r)\, \Psi^+(\mathbf{r})\, d\mathbf{r} \tag{35}$$

where

$$\Psi^+(\mathbf{r}') = e^{i\mathbf{k}\cdot\mathbf{r}'}$$

refers to the initial plane wave state and

$$\Psi_f^* = e^{-i\mathbf{k}'\cdot\mathbf{r}'}$$

the final state.

We shall now replace these by the relativistic spinor wavefunctions given in Eq. (32). One must remember that for both initial and final states, we are concerned only with the positive energy states, $\chi_\uparrow^+$ and $\chi_\downarrow^+$. Accordingly, we have for the initial states (putting $p_z = p$, $p_x = p_y = 0$)

$$\chi_{\uparrow \text{in}}^+ = N\begin{pmatrix} 1 \\ 0 \\ cp/(E_+ + mc^2) \\ 0 \end{pmatrix} e^{i\mathbf{k}\cdot\mathbf{r}} = N\begin{pmatrix} 1 \\ 0 \\ \beta\gamma/(\gamma+1) \\ 0 \end{pmatrix} e^{i\mathbf{k}\cdot\mathbf{r}} = u_1\, e^{i\mathbf{k}\cdot\mathbf{r}}$$

and

$$\chi_{\downarrow \text{in}}^+ = N\begin{pmatrix} 0 \\ 1 \\ 0 \\ -\beta\gamma/(\gamma+1) \end{pmatrix} e^{i\mathbf{k}\cdot\mathbf{r}} = u_2\, e^{i\mathbf{k}\cdot\mathbf{r}} \tag{36}$$

where we have written

$$p = m\beta\gamma, \quad E_+ = mc^2\gamma$$

with $\beta = v/c$ and $\gamma = 1/\sqrt{1-\beta^2}$ for convenience. For the final states, we set

$$p_z = p\cos\theta,\, p_x = p\sin\theta,\, p_y = 0$$

assuming, without loss of generality, that the scattering is in the $x - z$ plane. This gives

$$\chi^+_{\uparrow f} = N\begin{pmatrix}1\\0\\ \beta\gamma\cos\theta/(\gamma+1)\\ \beta\gamma\sin\theta/(\gamma+1)\end{pmatrix}e^{i\mathbf{k}'\cdot\mathbf{r}}$$

$$= v_1\, e^{i\mathbf{k}'\cdot\mathbf{r}}$$

and

$$\chi^+_{\downarrow f} = N\begin{pmatrix}0\\1\\ \beta\gamma\sin\theta/(\gamma+1)\\ -\beta\gamma\cos\theta/(\gamma+1)\end{pmatrix}e^{i\mathbf{k}'\cdot\mathbf{r}}$$

$$= v_2\, e^{i\mathbf{k}'\cdot\mathbf{r}} \tag{37}$$

Note that the magnitude p will be the same for both initial and final states for elastic scattering by a heavy scatterer. We shall now have to evaluate quantities such as

$$\int(\chi_f^\dagger)\, V(r)\, \chi_{\text{in}}\, d\mathbf{r}$$

As far as the integral over $d\mathbf{r}$ is concerned, Eq. (35) is unaltered and we obtain (writing $V = -Ze^2/r$)

$$f = \frac{mZe^2}{2\pi\hbar^2}\int\frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{r}\,d\mathbf{r} \tag{38}$$

where $\hbar\mathbf{q} = \hbar(\mathbf{k}' - \mathbf{k})$ is the momentum transfer (to the scatterer). This integral is not really well defined but it can be evaluated by inserting an integrating factor $e^{-\alpha r}$ in the integrand and, after carrying out the integration, letting α go to zero. Thus, we have

$$f = \frac{mZe^2}{2\pi\hbar^2}\int\frac{e^{i\mathbf{q}\cdot\mathbf{r}}\,e^{-\alpha r}}{r}\,d\mathbf{r}$$

an integral which has been carried out in Section 19.4.1. The answer is

$$f = \frac{2m}{\hbar^2}\,\frac{Ze^2}{\alpha^2 + q^2}$$

Putting $\alpha = 0$, we obtain

$$f = \frac{2m}{\hbar^2}\,\frac{Ze^2}{q^2} \tag{39}$$

We now have to multiply f by the spinor terms $v^\dagger u$ in order to obtain the scattering amplitudes. There are 4 of these, $v_1^\dagger u_1$, $v_1^\dagger u_2$, $v_2^\dagger u_1$ and $v_2^\dagger u_2$. We have to *average* over the initial unpolarized states, u_1 and u_2 and sum over the final states.

$$\frac{d\sigma}{d\Omega} = \left|\frac{2mZe^2}{q^2\hbar^2}\right|^2 \frac{1}{2}\left\{|v_1^\dagger u_1|^2 + |v_1^\dagger u_2|^2 + |v_2^\dagger u_1|^2| + |v_2^\dagger u_2|^2\right\}$$

The terms in the curly brackets give

$$2N^4\left\{\left[1 + \frac{\beta^2\gamma^2\cos\theta}{(1+\gamma)^2}\right]^2 + \left[\frac{\beta^2\gamma^2\sin\theta}{(1+\gamma)^2}\right]^2\right\}$$

$$= \frac{2N^4}{(1+\gamma)^4}\{(1+\gamma)^4 + 2(1+\gamma)^2\beta^2\gamma^2\cos\theta + \beta^4\gamma^4\}$$

It can be shown that

$$(1+\gamma)^4 + \beta^4\gamma^4 = 2(1+\gamma^2)(1+\gamma)^2$$

Also, writing $\cos\theta = 1 - 2\sin^2\theta/2$, we obtain

$$\frac{4N^4}{(1+\gamma)^2}\{1 + \gamma^2 + \beta^2\gamma^2(1 - 2\sin^2\theta/2)\} = \frac{8N^4\gamma^2}{(1+\gamma)^2}(1 - \beta^2\sin^2\theta/2)$$

This gives

$$\frac{d\sigma}{d\Omega} = \frac{(2m\,Ze^2)^2}{\hbar^2 q^2}\,\frac{4N^4\gamma^2}{(1+\gamma)^2}(1 - \beta^2\sin^2\theta/2)$$

Before inserting the value of N, we must note that we should normalize the spinor functions in such a way that the probability $\int\psi^\dagger\psi d\tau$ is invariant. Since the volume element $d\tau$ contracts by γ, this means that we must take*

$$N = \sqrt{\gamma}\left[1 + \frac{c^2p^2}{E + mc^2}\right]^{-1/2} = \sqrt{\frac{\gamma+1}{2}}$$

Thus

$$\frac{d\sigma}{d\Omega} = \left(\frac{2mZe^2}{\hbar^2q^2}\right)^2\gamma^2(1 - \beta^2\sin^2\theta/2)$$

Now

$$\hbar^2q^2 = h^2(\mathbf{k}' - \mathbf{k})^2 - 4\hbar^2k^2\sin^4\theta/2 \equiv 4p^2\sin^2\theta/2$$

This gives

$$\frac{d\sigma}{d\Omega} = \frac{m^2Z^2e^2}{4p^4\sin^4\theta/2}\gamma^2(1 - \beta^2\sin^2\theta/2)$$

$$= \left(\frac{Ze^2}{2pv}\right)^2\frac{(1 - \beta^2\sin^4\theta/2)}{\sin^4\theta/2} \tag{40}$$

---

*See Solution 23.9.

a formula which evidently goes over to the Rutherford formula in the nonrelativistic limit.*

23.8. The Election in an Electromagnetic Field

We modify the Dirac equation simply by replacing the operators

$$\mathbf{p} \text{ by } \mathbf{p} - \frac{e\mathbf{A}}{c}$$

and

$$E \text{ by } E - e\phi$$

where A and ϕ are the vector and scalar potentials. Both these replacements can be concisely expressed in four-dimensional form

$$p_\mu \to p_\mu - \frac{eA_\mu}{c}$$

with

$$p_4 = iE/c \quad \text{and} \quad A_4 = i\phi \tag{41}$$

The solutions will no longer be of the plane wave form [(34)]. We, therefore, cannot separate out the solutions, as we did in Sec. 23.6, into a part χ independent of space-time coordinates. However, we still write

$$\psi(\mathbf{r}, t) = \begin{pmatrix} u(\mathbf{r}, t) \\ v(\mathbf{r}, t) \end{pmatrix} \tag{42}$$

and remember that the spinors u and v now incorporate the space-time dependence. We now have the equations [similar to Eqs. (29)]

$$c\sigma \cdot \left(\mathbf{p} - \frac{e\mathbf{A}}{c}\right) v = (E - e\phi - mc^2)\, u \tag{43}$$

and

$$c\sigma \cdot \left(\mathbf{p} - \frac{e\mathbf{A}}{c}\right) u = (E - e\phi + mc^2)\, v \tag{44}$$

the major difference being that we have *not carried out the operations with p and E.*

We are interested in positive energy solutions

$$E = mc^2 + \varepsilon \tag{45}$$

We obtain from (44)

$$c\sigma \cdot \left(\mathbf{p} - \frac{e\mathbf{A}}{c}\right) u = (2mc^2 + \varepsilon - e\phi)\, v \tag{46}$$

---

*Compare this result with Eq. (116) of Chapter 19.

For *small* ε and ϕ we may write

$$v \approx \frac{1}{2mc}\,\sigma\cdot\left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right)u$$

Substituting this into Eq. (43), we obtain

$$\frac{1}{2m}\left[\sigma\cdot\left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right)\right]^2 u = (\varepsilon - e\phi)\,u \tag{47}$$

Using the relation

$$(\sigma\cdot\mathbf{B})\,(\sigma\cdot\mathbf{C}) = \mathbf{B}\cdot\mathbf{C} + i\sigma\cdot(\mathbf{B}\times\mathbf{C}) \tag{48}$$

we have

$$\left[\sigma\cdot\left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right)\right]^2 = \left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right)^2 + i\sigma\cdot\left\{\left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right)\times\left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right)\right\} \tag{49}$$

Since **p** is an operator, the vector product in the last term does not vanish. Indeed, we have

$$\begin{aligned}\left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right)\times\left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right) &= -\frac{e}{c}\,(\mathbf{A}\times\mathbf{p}+\mathbf{p}\times\mathbf{A})\\ &= \frac{ie\hbar}{c}\,\nabla\times\mathbf{A} = \frac{ie\hbar}{c}\,\mathbf{H}\end{aligned}$$

where $\mathbf{H} = \nabla\times\mathbf{A}$ is the magnetic field. Thus Eq. (47) gives

$$\left\{\frac{1}{2m}\left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right)^2 - \frac{e\hbar}{2mc}\,\sigma\cdot\mathbf{H} + e\phi\right\}u = \varepsilon u \tag{50}$$

This is the Pauli equation discussed in Chapter 18. It is very similar to the nonrelativistic Schrödinger equation with one important extra term. This term suggests that the electron, in a magnetic field, acquires an extra energy $-\mu\cdot\mathbf{H} = -(e\hbar/2mc)\,\sigma\cdot\mathbf{H}$ so that it behaves as if it has a magnetic moment μ associated with its spin, namely

$$\mu = \frac{e\hbar}{2mc}\,\sigma = \mu_B\sigma \tag{51}$$

Our convention is that e is the actual charge; for the electron we must put $e = -4.8\times10^{-10}$ (esu) μ_B is the Bohr magneton.

Thus, the Dirac equation predicts that for a spin $\frac{1}{2}$ particle, the magnetic moment is always given by the relation (51). While this prediction is in very good agreement with experiment it fails badly for the proton and the neutron. It is possible to modify the equation keeping it relativistically invariant by introducing, *ad hoc*, an extra term that accounts for the anomalous magnetic moment of these particles.*

---

*For details, see Davydov (1965).

Another new feature that may be expected is the interaction between the spin and orbital motions. We examine the higher order corrections to the Pauli equation in an electrostatic field.* Writing $\mathbf{A} = 0$ we obtain from Eqs. (43) and (44)

$$c\,(\sigma \cdot \mathbf{p})\, v = (\varepsilon - e\phi)\, u \tag{52}$$

$$c\,(\sigma \cdot \mathbf{p})\, u = (2mc^2 + \varepsilon - e\phi)\, v \tag{53}$$

The charge density is

$$\rho = \psi^\dagger \psi = u^\dagger u + v^\dagger v$$

From (53), we have

$$v \approx \frac{1}{2mc}\, \sigma \cdot \mathbf{p} u \tag{54}$$

so that

$$v^\dagger v \approx u^\dagger \frac{p^2}{4m^2c^2}\, u$$

This gives $\rho = u^\dagger\,(1 + p^2/4m^2c^2)\, u$ (to order v^2/c^2) which suggests that to this order we *cannot* regard u as the wavefunction in the non-relativistic approximation. Instead, if we take

$$u' = \left(1 + \frac{p^2}{8m^2c^2}\right) u$$

and

$$u = \left(1 - \frac{p^2}{8m^2c^2}\right) u' \tag{55}$$

then $\rho = (u')^\dagger u'$ to order v^2/c^2 so that it is u' that we want for the wavefunction. Our aim is to solve for v, for which we substitute in Eq. (52) and use Eqs. (55) to change to u', taking care to retain terms up to order $1/c^2$. From Eq. (53b), we have

$$c\sigma \cdot \mathbf{p} u = (2mc^2)\, v + (\varepsilon - e\phi)\, \frac{\sigma \cdot \mathbf{p}}{2mc}\, u$$

where in the term multiplying $(\varepsilon - e\phi)$, which is small, we have used the lower approximation (54) for v. Thus

$$v = \frac{1}{2mc}\left(1 - \frac{\varepsilon - e\phi}{2mc^2}\right) \sigma \cdot \mathbf{p} u$$

---

*We follow the treatment of Berestetskii, Lifshitz and Pitaavskii (1971).

Substituting this into Eq. (52), we obtain

$$
\begin{aligned}
(\varepsilon - e\phi)\, u &= \frac{1}{2m}\, (\sigma \cdot \mathbf{p}) \left(1 - \frac{\varepsilon - e\phi}{2mc^2}\right) \sigma \cdot \mathbf{p}u \\
&= \frac{1}{2m}\left[\, p^2 - \frac{\varepsilon}{2mc}\, p^2 + \frac{e}{2mc^2}\, (\sigma \cdot \mathbf{p})\, \phi\, (\sigma \cdot \mathbf{p}) \,\right] u
\end{aligned}
$$

Rearranging terms, this gives

$$
\varepsilon \left(1 + \frac{p^2}{4m^2c^2}\right) u = \left[e\phi + \frac{1}{2m} \left\{ p^2 + \frac{e}{2mc}\, (\sigma \cdot \mathbf{p})\, \phi\, (\sigma \,.\, \mathbf{p}) \right\} u \,\right]
$$

We multiply this on the left by $1 - p^2/8m^2c^2$, retain terms up to $1/c^2$ and use Eq. (55)

$$
\varepsilon u' = \left(1 - \frac{p^2}{8m^2c^2}\right)\left[e\phi + \frac{p^2}{2m} + \frac{e}{4m^2c^2}\, (\sigma \cdot \mathbf{p})\, \phi\, (\sigma \cdot \mathbf{p}) \right]\left(1 - \frac{p^2}{8m^2c^2}\right) u' \tag{56}
$$

Eq. (56) gives us the required eigenvalue relation

$$
\varepsilon u' = Hu'
$$

Retaining terms up to the order $1/c^2$, we have

$$
H = e\phi + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} - \frac{e}{8m^2c^2}\, (p^2\phi + \phi p^2) + \frac{e}{4m^2c^2}\, (\sigma \cdot \mathbf{p})\, \phi\, (\sigma \cdot \mathbf{p})
$$

Now

$$
\begin{aligned}
(\sigma \cdot \mathbf{p})\, \phi\, (\sigma \cdot \mathbf{p}) &= \phi\, (\sigma \cdot \mathbf{p})\, (\sigma \cdot \mathbf{p}) + (\sigma \cdot \mathbf{p}\phi)\, (\sigma \cdot \mathbf{p}) \\
&= \phi p^2 + i\hbar\, (\sigma \cdot \mathbf{E})\, (\sigma \cdot \mathbf{p}) \\
&= \phi p^2 + i\hbar\, [\mathbf{E} \cdot \mathbf{p} + i\sigma \cdot \mathbf{E} \times \mathbf{p}]
\end{aligned} \tag{57}
$$

where

$\mathbf{E} = -\,\nabla\phi$ is the electric field.

We also have

$$
\begin{aligned}
(p^2\phi - \phi p^2)\, u' &= -\,\hbar^2\, [\nabla^2\, (\phi u') - \phi\nabla^2 u'] \\
&= -\,\hbar^2\, [\nabla \cdot (u'\nabla\phi) + \phi\nabla u' - \phi\nabla^2 u'] \\
&= -\,\hbar^2\, [2\nabla\phi \cdot \nabla + (\nabla^2\phi)]\, u'
\end{aligned}
$$

Writing this in terms of E and p, we obtain

$$
p^2\phi - \phi p^2 = 2i\hbar\, \mathbf{E} \cdot \mathbf{p} + \hbar^2\nabla \cdot \mathbf{E} \tag{58}
$$

Substituting (43) and (44) into the expression for H, we obtain

$$
H = e\phi + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} - \frac{e\hbar}{4m^2c^2}\, \sigma \cdot \mathbf{E} \times \mathbf{p} - \frac{e\hbar}{8m^2c^2}\, \nabla \cdot \mathbf{E} \tag{59}
$$

The first two terms are the usual non-relativistic terms. The third term is the kinetic energy correction up to order $1/c^2$ as may be seen by expanding $mc^2\,(1+p^2/m^2c^2)^{1/2} - mc^2$. The fourth term is the spin-orbit interaction energy. The nomenclature may be understood if we take the example of the field to a point charge when $\mathbf{E} \sim \mathbf{r}/r^3$. This gives a term proportional to $\sigma \cdot \mathbf{l} \sim \mathbf{s} \cdot \mathbf{l}$ where $\mathbf{s}$ is the spin and $\mathbf{l}$, the orbital angular momentum. The last term is a correction to the potential energy $e\phi$, called the Darwin term.*

23.9 Central Potential

Let us now consider the solution of the Dirac equation for a particle in a central potential $V(r)$. The Hamiltonian is

$$H = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V(r) = H_0 + V(r)$$

It can be shown that the free particle Hamiltonian H_0 does not commute with the orbital angular momentum $\mathbf{L}$ (See Problem 23.2). However, it does commute with $\mathbf{J} = \mathbf{L} + \mathbf{s}$. Here

$$\hbar\mathbf{s} = \frac{1}{2}\,\hbar\,\Sigma = \frac{1}{2}\,\hbar\begin{pmatrix}\sigma & 0\\ 0 & \sigma\end{pmatrix} \tag{60}$$

For the central potential the Hamiltonian still commutes with $\mathbf{J}$ and J^2 so that eigenfunctions can be conveniently chosen so that they belong to definite states of J^2 and J_z. We label these states by j and m, the eigenvalue of $\mathbf{J}^2$ is $j\,(j+1)\,\hbar^2$ and of J_z is $m\hbar$ for the particular state. A particular value of J can arise from the combinations $l - \frac{1}{2}$ or $l + \frac{1}{2}$ of the orbital and spin parts, the two states having opposite parities.

We shall proceed by separating the variables in spherical polar coordinates, the appropriate coordinates in view of the spherical symmetry of $V(r)$. To do this, it is convenient to introduce the radial 'momentum' and velocity operators,

$$p_r = \frac{1}{r}\,(\mathbf{r}\cdot\mathbf{p} - i\hbar) = \left(\frac{i\hbar}{r}\; r\,\frac{\partial}{\partial r} + 1\right) \text{ and } \alpha_r = \frac{1}{r}\,(\boldsymbol{\alpha}\cdot\mathbf{r}) \tag{61}$$

Note that

$$\alpha_r^2 = 1$$

Using the relation (Problem 23.4)

$$(\boldsymbol{\alpha}\cdot\mathbf{B})\,(\boldsymbol{\alpha}\cdot\mathbf{C}) = \mathbf{B}\cdot\mathbf{C} + i\,\Sigma\cdot(\mathbf{B}\times\mathbf{C}) \tag{62}$$

and putting $\mathbf{B} = \mathbf{r}$, $\mathbf{C} = \mathbf{p}$, we obtain

$$\begin{aligned}(\boldsymbol{\alpha}\cdot\mathbf{r})\,(\boldsymbol{\alpha}\cdot\mathbf{p}) &= rp_r + i\hbar + i\Sigma\cdot(\mathbf{r}\times\mathbf{p})\\ &= rp_r + i\hbar\,(\Sigma\cdot\mathbf{L} + 1)\end{aligned} \tag{63}$$

---

*The spin-orbit term is the form $-\frac{1}{2}\,\mu\cdot\mathbf{E}\times\mathbf{v}/c$; in the rest frame of the particle this would appear to give the strange result $-\frac{1}{2}\,\mu\cdot\mathbf{H}$ which is "off" by a factor $\frac{1}{2}$; however expression (59) is the correct one and is due to the so called Thomas precession. For an explanation of this effect and the Darwin term, see Baym (1969).

using the definition $\mathbf{L} = \hbar\,(\mathbf{r} \times \mathbf{p})$. Thus

$$r\alpha_r\,\boldsymbol{\alpha}\cdot\mathbf{p} = rp_r + i\hbar\,(\boldsymbol{\Sigma}\cdot\mathbf{L} + 1)$$

Multiplying by α_r/r on the left, we obtain

$$\boldsymbol{\alpha}\cdot\mathbf{p} = \alpha_r p_r + i\hbar\,\frac{\alpha_r}{r}\,(\boldsymbol{\Sigma}\cdot\mathbf{L} + 1) \tag{64}$$

It is convenient to introduce the operator

$$K = \beta\,(\boldsymbol{\Sigma}\cdot\mathbf{L} + 1) \tag{65}$$

It is easily shown that this commutes with the Hamiltonian. (This is the reason for the β in the definition of K)

$$K^2 = [\beta\,(\boldsymbol{\Sigma}\cdot\mathbf{L} + 1)]^2 = (\boldsymbol{\Sigma}\cdot\mathbf{L} + 1)^2$$

(since β commutes with Σ)

$$= (\boldsymbol{\Sigma}\cdot\mathbf{L})^2 + 2\boldsymbol{\Sigma}\cdot\mathbf{L} + 1$$

Now

$$(\boldsymbol{\Sigma}\cdot\mathbf{L})^2 = L^2 - \boldsymbol{\Sigma}\cdot\mathbf{L}$$

using Eq. (62) and

$$\boldsymbol{\Sigma}\times\boldsymbol{\Sigma} = i\boldsymbol{\Sigma}$$

Thus

$$\begin{aligned} K^2 &= L^2 + \boldsymbol{\Sigma}\cdot\mathbf{L} + 1 \\ &= \left(\mathbf{L} + \frac{\boldsymbol{\Sigma}}{2}\right)^2 + \frac{1}{4} = J^2 + \frac{1}{4} \end{aligned} \tag{66}$$

since the eigenvalue of Σ^2 is 2. The eigenvalues of K^2 are, therefore,

$$j(j+1) + \tfrac{1}{4} = (j + \tfrac{1}{2})^2$$

Since K commutes with the Hamiltonian, we can set up a representation in which K and H are diagonal. Now

$$H = c\alpha_r p_r = \frac{i\hbar c}{r}\,\alpha_r\beta K + \beta mc^2 + V(r) \tag{67}$$

We can now choose (matrix) representations of α_r and β which satisfy the conditions

$$\alpha_r^2 = \beta^2 = 1 \quad\text{and}\quad [\alpha_r, \beta] = 0 \tag{68}$$

A simple one is $\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ and $\alpha_r = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$. Writing $\psi = \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix}$, the relation $H\psi = E\psi$ gives the two coupled equations

$$(E - mc^2 - V)\,\psi_a + \left(icp_r + \frac{\hbar c}{r}K\right)\psi_b = 0 \tag{69}$$

and

$$(E + mc^2 - V)\,\psi_b - \left(icp_r - \frac{\hbar c}{r}K\right)\psi_a = 0 \tag{70}$$

The angle and spin dependent parts are included in K. If we choose ψ_a, ψ_b to be eigenfunctions of K (with eigenvalue denoted by the same symbol K), then in Eqs. (69) and (70), we need only concern ourselves with the radial parts of ψ_a and ψ_b. We set

$$\psi_a = \frac{F}{r},\ \psi_b = \frac{G}{r} \tag{71}$$

Noting that

$$p_r\left(\frac{F}{r}\right) = -\frac{i\hbar}{r}\left(r\frac{\partial}{\partial r} + 1\right)\left(\frac{F}{r}\right) = -\frac{i\hbar}{r}\frac{dF}{dr}\ \text{etc.}$$

we obtain

$$(E - mc^2 - V)\,F + \hbar c\left(\frac{dG}{dr} + \frac{KG}{r}\right) = 0 \tag{72}$$

and

$$(E + mc^2 - V)\,G + \hbar c\left(\frac{dF}{dr} - \frac{KF}{r}\right) = 0 \tag{73}$$

23.10 Energy Levels of the Hydrogen Atom

For the hydrogenlike atom, we set $V(r) = -Ze^2/r$. Before trying a series solution of Eqs. (72) and (73) let us look at the asymptotic behaviour of F and G. We may write (as $r \to \infty$),

$$(E - mc^2)\,F + \hbar c\,\frac{dG}{dr} = 0$$

$$(E + mc^2)\,G - \hbar c\,\frac{dF}{dr} = 0$$

whence

$$\frac{d^2F}{dr^2} - \frac{m^2c^4 - E^2}{(\hbar c)^2}F = 0 \tag{74}$$

Since we expect, for the bound state, $F \to 0$ as $r \to \infty$, we must have $mc^2 > |E|$.* (For positive energies, this merely states that we expect the total energy of the atom to be somewhat less than the rest energy of the electron; one must not forget that we have not included the rest energy of the proton in the Hamiltonian in the first place). Thus, the asymptotic behaviour is

$$F, G \sim e^{-\rho} \tag{75}$$

---

*Otherwise, the solution to Eq. (74) will be oscillatory.

where

$$\rho = \frac{\sqrt{m^2c^4 - E^2}}{\hbar c}\, r \tag{76}$$

is an obviously convenient dimensionless variable. Eqs. (72) and (73) become

$$\left(-\nu + Z\frac{\alpha}{\rho}\right)F + \frac{dG}{d\rho} + \frac{KG}{\rho} = 0 \tag{77}$$

$$\left(\frac{1}{\nu} + Z\frac{\alpha}{\rho}\right)G - \frac{dF}{d\rho} + \frac{KG}{\rho} = 0 \tag{78}$$

where we have put

$$\sqrt{\frac{mc^2 - E}{mc^2 + E}} = \nu,\ \frac{e^2}{\hbar c} = \alpha \tag{79}$$

The asymptotic forms (75) suggest a solution of the following form

$$F(\rho) = f(\rho)\, e^{-\rho},\ G(\rho) = g(\rho)\, e^{-\rho} \tag{80}$$

so that we have

$$\left(-\nu + \frac{Z\alpha}{\rho}\right)f + \left(\frac{d}{d\rho} + \frac{K}{\rho} - 1\right)g = 0 \tag{81}$$

$$\left(\frac{1}{\nu} + \frac{Z\alpha}{\rho}\right)g - \left(\frac{d}{d\rho} - \frac{K}{\rho} - 1\right)f = 0 \tag{82}$$

Substituting

$$f(\rho) = \rho^s \sum_{j=0}^{\infty} a_j\rho^j,\ g(\rho) = \rho^s \sum_{j=0}^{\infty} b_j\rho^j \tag{83}$$

and comparing the coefficients of ρ^{s+j-1}, we shall get the following indicial equations.

$$-\nu a_{j-1} + Z\alpha a_j + (j + s)\, b_j + Kb_j - b_{j-1} = 0 \tag{84}$$

$$\frac{1}{\nu}\, b_{j-1} + Z\alpha b_j - (j + s)\, a_j + Ka_j + a_{j-1} = 0 \tag{85}$$

From the coefficients of the lowest term ρ^{s-1}, we obtain

$$Z\alpha a_0 + (s + K)\, b_0 = 0 \text{ and } Z\alpha b_0 - (s - K)\, a_0 = 0 \tag{86}$$

Since a_0 and b_0 are not zero, we must have

$$s^2 = K^2 - Z^2\alpha^2$$

$$\text{or} \quad s = \sqrt{K^2 - Z^2\alpha^2} \tag{87}$$

where the positive root is chosen to keep the functions F and G regular at the origin.

Multiplying Eq. (85) by ν and adding it to Eq. (84) we obtain

$$a_j\,[(j + s - K) - Z\alpha] = b_j\,[(j + s + K) + Z\alpha] \tag{88}$$

It can be shown, as was done for the Schrödinger equation solution of the hydrogen atom, that if we let the series (83) go to an infinite number of terms, the functions $f(\rho)$ and $g(\rho)$ will behave like $e^{2\rho}$ so that the solutions $F(\rho)$ and $G(\rho)$ will diverge. We must, therefore, assume that $j = n'$, where n' is a fixed integer, the series terminates and $a_{n'+1} = 0$ [and hence $b_{n'+1} = 0$, according to Eq. (88)]. Setting $j = n' + 1$ in Eqs. (84) and (85), we obtain

$$-\nu\, a_{n'} - b_{n'} = 0 \quad \text{or} \quad b_{n'} = -\nu a_{n'} \tag{89}$$

using Eq. (88), with $j = n'$, we obtain

$$(n' + s - K) - Z\alpha = -\nu\,[(n' + s + K) + Z\alpha] \tag{90}$$

or

$$\begin{aligned} 2\nu\,(n' + s) &= Z\alpha\,(1 - \nu^2) \\ &= \frac{Z\alpha\, 2E}{mc^2 + E} \end{aligned}$$

remembering that $\nu^2 = (mc^2 - E)/(mc^2 + E)$. Squaring, we have $(m^2c^4 - E^2)(n' + s)^2 = Z^2\alpha^2E^2$. This gives

$$E = mc^2\left[1 + \frac{Z^2\alpha^2}{(n' + s)^2}\right]^{-1/2} \tag{91}$$

α here, it may be recalled, is the fine structure constant,

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}\cdot$$

Now, the eigenvalues of K^2 are $(j + \frac{1}{2})^2$ so that $s = \sqrt{(j + \frac{1}{2})^2 - Z^2\alpha^2}$. To appreciate the change from the non-relativistic theory, let us introduce the small number

$$\varepsilon_j = (j + \tfrac{1}{2}) - \sqrt{(j + \tfrac{1}{2})^2 - Z^2\alpha^2}$$

so that $s = j + \frac{1}{2} - \varepsilon$. We also introduce the principal quantum number

$$n = j + \tfrac{1}{2} + n' \left(\begin{matrix} n = 1,2,3,\ldots \\ j = \frac{1}{2}, \frac{3}{2}, \ldots, n - \frac{1}{2} \end{matrix}\right)$$

Thus $n' + s = n - \varepsilon_j$, so that

$$E = mc^2\left[1 + \frac{Z^2\alpha^2}{(n - \varepsilon_j)^2}\right]^{-1/2} \tag{92}$$

Remembering that ε_j is also a function of $Z^2\alpha^2$, one can expand E as a power series in $Z^2\alpha^2$ to obtain (See Problem 23.10)

$$E_{n,j} = mc^2\left[1 - \frac{Z^2\alpha^2}{2n^2} - \frac{Z^4\alpha^4}{2n^4}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right] \tag{93}$$

Apart from the constant mass term, the second term in Eq. (93) is identical to the non-relativistic expression while the third gives the relativistic corrections. Labelling the energy levels as

$2S_{1/2}$ (for $n = 2, j = 1/2$ and $l = 0$)
$2P_{1/2}$ ($n = 2, j = 1/2, l = 1$)
$2P_{3/2}$ ($n = 2, j = 3/2, l = 1$)

We note that, while non-relativistic theory predicts that these three states are all degenerate, Eq. (93) predicts that only $2S_{1/2}$ and $2P_{1/2}$ are degenerate while $2P_{3/2}$ lies lower by about 10^{-4} eV.

In 1947, a crucial experiment by Lamb and Rutherford established that $2S_{1/2}$ lies about 1058MHz below $2P_{1/2}$ (the frequency ν corresponds to the energy difference $h\nu \sim 4.4 \times 10^{-9}$ eV). Although this might appear a very small discrepancy this experiment initiated very important developments which led to a consistent theory of quantum electrodynamics.*

23.11 The Hole Theory and Positrons

We have seen that the Dirac equation admits both positive and negative energy solutions. In the presence of a field one would expect the electron to make radiative transitions to a negative energy state in fact, to $E = -\infty$. There are other difficulties with negative energies. An electron at rest in a negative energy state has a negative rest mass. Clearly, such electrons would move opposite to an applied force. The theory presented, so far, is thus an incomplete *physical* theory.

Dirac made a remarkable suggestion to avoid these difficulties. He assumed that all the negative energy states are normally occupied by electrons; i.e., vacuum is the state of fully occupied negative energy states and empty positive ones. An electron with positive energy now introduced into this system is prevented from making a transition to a negative energy state because of the exclusion principle. In vacuum, one therefore has this negative energy 'sea' of electrons giving an infinite charge density. Dirac, therefore, made a further assumption, namely, that electrons filling up negative energy states do not contribute to the external field, the total energy and momentum of the system. Only *departures* from the distribution in a vacuum will contribute to observable quantities.

To see how this works, suppose a negative energy electron with an energy $-|E_i|$ and momentum $\mathbf{p}$ is removed from the negative energy sea, under the action of an external field, to a positive energy state (see Fig. 23.1).

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* For a simple picture of the origin of the Lamb Shift see Bjorken and Drell (1964) Ch. 4.

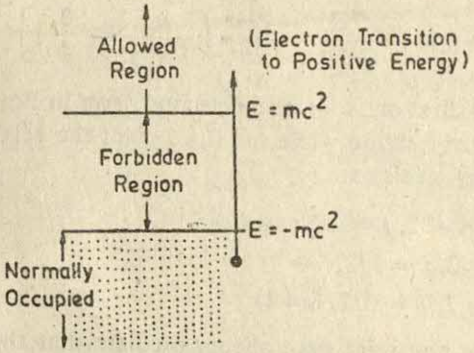

Fig. 23.1

The system (the sea) is now *deficient in energy* $-|E_i|$ and momentum $\mathbf{p}$. This means that the residual sea behaves as though it has a *hole* with energy $|E_i|$ and momentum $-\mathbf{p}$. (Notice that the hole has *positive* energy $|E_i|$.) Also, with the removal of charge $-e$, the net effect of the hole is that of a positive charge $+e$. This hole, therefore, behaves like a particle with the electronic mass m and charge e and is interpreted as a *positron.**†

If the external field removes an electron of momentum $\mathbf{p}_i$ from a negative energy state $-|E_i|$ to a state of momentum $\mathbf{p}_f$ and positive energy $+|E_f|$, then the hole will have an energy $+|E_i|$ and momentum $-\mathbf{p}_i$. In other words, the final system now consists of an electron of energy $|E_f|$ and momentum $\mathbf{p}_f$ and a positron of energy $|E_i|$ and momentum $-\mathbf{p}_i$. Clearly, the total energy $|E_i|+|E_f|$ and the total momentum $\mathbf{p}_f-\mathbf{p}_i$ of the two particles in the final states must have been supplied by the external field. Moreover, since

$$|E_i|+|E_f| > 2mc^2$$

this is the minimum required energy for this process, called *pair production*. Thus, the hole theory provides a simple explanation for the positron and phenomena such as the creation or annihilation of pairs.

However what has been gained in interpretation has made the theory far more complicated. Electron-electron scattering, for example, is no longer to be thought of a simple two body process. The vacuum**, with its infinite number of particles can participate in the phenomenon making the theory a many-body one. While it is true that for low energies generally the situation is not as drastic, nevertheless one should expect new phenomena to manifest themselves. For example, the electromagnetic field can *polarise* the vacuum (somewhat like the polarization of a dielectric). Vacuum polarization produces observable effects; for example, in the hydrogen atom it reduces the Lamb shift $(2S_{1/2} - 2P_{1/2})$ by about 27 *MHz* in agreement with experiment.

---

*All observed states are states of positive energy. When making calculations for physical quantities it is necessary to select out final states of positive energy.

†The hole theory treats the positron on a different footing (at least in the physical interpretation) from the electron. Modern theories of quantum electrodynamics have avoided this distinction.

**Dirac's original idea of the particle as an excitation of the strange 'vacuum' has been very fruitful and the idea is exploited in the theory of condensed states. (See Kaempffer, *Concepts in Quantum Mechanics*, Academic Press, New York, 1965).

PROBLEMS

PROBLEM 23.1

Show that the four spinors described by (32) are orthonormal, i.e.,

$$\chi_a^\dagger \chi_b = \delta_{ab}$$

where $\chi_a^\dagger$, χ_b are any two of them.

PROBLEM 23.2

Show that $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ does not commute with the free particle Dirac Hamiltonian, while $\mathbf{J} = \mathbf{L} + \mathbf{s}$ does and hence $\mathbf{J}$ is a constant of the motion. Here $\mathbf{s} = \frac{1}{2}\hbar\Sigma$ where

$$\Sigma = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix}$$

PROBLEM 23.3

Show that the complex conjugate of Dirac equation can be written as

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial x_\mu} + \frac{e}{c}A_\mu\right)\bar{\psi}\gamma_\mu + imc\bar{\psi} = 0$$

PROBLEM 23.4

Prove Eq. (62):

$$(\alpha \,.\, \mathbf{B})(\alpha \cdot \mathbf{C}) = (\mathbf{B} \cdot \mathbf{C}) + i\Sigma \cdot (\mathbf{B} \times \mathbf{C})$$

PROBLEM 23.5

Verify that the rate of change of position operator (in the Heisenberg picture) is given by

$$\frac{d\mathbf{r}}{dt} = c\alpha$$

Discuss this result.

PROBLEM 23.6

(a) Show that the Dirac equation for an electron in a field

$$\left[\gamma_\mu\left(p_\mu - \frac{eA_\mu}{c}\right) - imc\right]\psi = 0 \tag{94}$$

is invariant under the gauge transformations

$$A_\mu = A_{\mu'} + \frac{\partial f}{\partial x_\mu}$$

and

$$\psi = \psi' \exp [ief/\hbar c] \tag{95}$$

Here $f(x_\mu)$ satisfies the relation $\partial^2 f/\partial x_\mu^2 = 0$.

(b) Show that the addition of a term of the form $a\gamma_\mu \gamma_\nu F_{\mu\nu} \psi$ in (94) will still leave the equation gauge invariant.

Here

$$F_{\mu\nu} = \frac{\partial A_\nu}{\partial x_\mu} - \frac{\partial A_\mu}{\partial x_\nu}$$

Problem 23.7

Assume that the frame Σ' introduced in Sec. 23.5 is obtained by a simple rotation of Σ about the z-axis by an angle φ. Show that the following matrix S satisfies the relation (23).

$$S = \exp\left[\frac{i\varphi}{2}\sigma_{12}\right]$$

where

$$\sigma_{12} = i/2\,[\gamma_1, \gamma_2] = i\gamma_1\gamma_2$$

Problem 23.8

Suppose Σ' moves along the x-axis with respect to Σ with a velocity βc. Show that the matrix S is given by

$$S = \exp\left[\frac{i\varphi}{2}\sigma_{14}\right], \sigma_{14} = i\gamma_1\gamma_4$$

writing

$\varphi = i\theta$, show that $\tanh\theta = \beta$.

Problem 23.9

Starting from spinors for a particle at rest

$$\begin{pmatrix}1\\0\\0\\0\end{pmatrix}, \begin{pmatrix}0\\1\\0\\0\end{pmatrix}, \begin{pmatrix}0\\0\\1\\0\end{pmatrix}, \begin{pmatrix}0\\0\\0\\1\end{pmatrix}.$$

apply the transformation S of Problem 23.8 to find the solutions for a particle travelling in the x-direction with velocity βc.

Problem 23.10

Obtain the expression (93) by expanding (92) up to order α^4.

Problem 23.11

Discuss the problem of pair annihilation from the point of view of hole theory. Is this process possible in vacuum?

SOLUTIONS

SOLUTION 23.2

We consider first $[L_x, H]$. This is

$$\begin{aligned} c\alpha \cdot [(yp_z - zp_y)\,\mathbf{p} - \mathbf{p}\,(yp_z - zp_y)] \\ &= c\alpha_2\,(yp_y - p_y y)\,p_z + c\alpha_3\,(-zp_z + p_z z)p_y \\ &= ic\hbar\,(\alpha_2 p_z - \alpha_3 p_y) \end{aligned} \tag{96}$$

To calculate $[\Sigma_x, H]$, we note that

$$\Sigma_x = \begin{pmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{pmatrix} \text{ and } \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}$$

so that

$$\Sigma_x\alpha_2 - \alpha_2\Sigma_x = 2i\alpha_3$$

and $\quad \Sigma_x\alpha_3 - \alpha_3\Sigma_x = -2i\alpha_2$

This gives

$$\begin{aligned} [\Sigma_x, H] &= ic\,(\alpha \cdot \mathbf{p}\Sigma_x - \Sigma_x\alpha \cdot \mathbf{p}) \\ &= 2ic\,(\alpha_3 p_y - \alpha_2 p_z) \end{aligned} \tag{97}$$

Thus $J_x = L_x + \frac{1}{2}\hbar\Sigma_x$ (and similarly other components) commutes with H.

SOLUTION 23.3

In a field, Eq. (11) is modified to

$$\left\{\gamma_\mu\left(p_\mu - \frac{eA_\mu}{c}\right) - imc\right\}\psi = 0 \tag{98}$$

Writing out the space and time components separately,

$$\frac{\hbar}{i}\left(\gamma_j\,\frac{\partial\psi}{\partial x_j} + \gamma_4\,\frac{\partial\psi}{\partial x_4}\right) - \frac{e}{c}\,\gamma_j A_j\psi - \frac{e}{c}\,\gamma_4 A_4\psi - imc\psi = 0$$

Remembering that $x_4^* = -x_4$, $A_4^* = -A_4$ and $\gamma_\mu{}^\dagger = \gamma_\mu$, we obtain for the adjoint equation,

$$-\frac{\hbar}{i}\left(\frac{\partial\psi^\dagger}{\partial x_j}\,\gamma_j - \frac{\partial\psi^\dagger}{\partial x_4}\,\gamma_4\right) - \frac{e}{c}\,\psi^\dagger\gamma_j A_j + \frac{e}{c}\,\psi^\dagger\gamma_4 A_4 + imc\psi^\dagger = 0$$

Writing $\psi^\dagger = \bar{\psi}\gamma_4$ and $\gamma_4\gamma_j = -\gamma_j\gamma_4$ and multiplying by γ_4 on the right, we obtain

$$\left(\frac{\hbar}{i}\,\frac{\partial}{\partial x_\mu} + eA_\mu\right)\bar{\psi}\gamma_\mu + imc\,\bar{\psi} = 0$$

or

$$\left\{\left(p_\mu + \frac{e}{c}\,A_\mu\right)\gamma_\mu + imc\right\}\bar{\psi} = 0 \tag{99}$$

This result is sometimes expressed concisely in Feynman notation as

$$\bar{\psi}\left(\overleftarrow{\not p} + \frac{e}{c}\not a + imc\right) = 0 \tag{100}$$

The arrow on top of p is to remind us that the derivatives p operate on ψ, but p has to be on the right of $\bar{\psi}$ in order to keep the order of matrix multiplication of $\bar{\psi}$ and γ_μ right.

Solution 23.5

From Heisenberg's equation, we have

$$\frac{d\mathbf{r}}{dt} = \frac{i}{\hbar}[\mathrm{H}, \mathbf{r}]$$

We have

$$\frac{dx}{dt} = \frac{i}{\hbar} c[\alpha \cdot \mathbf{p}x - x\alpha \cdot \mathbf{p}]$$

We need only consider $\alpha_x p_x$ in $\alpha \cdot \mathbf{p}$, the rest commute. Thus

$$\frac{dx}{dt} = \frac{ic}{\hbar}\alpha_x(p_x x - xp_x) = c\alpha_x$$

Since the eigenvalues of α_x are ± 1, $\pm c$ are the only possible eigenvalues of each of the operators $d\mathbf{r}/dt$.

A precise velocity measurement requires the precise measurement of position at two different times which means the uncertainties in momenta approach infinity. In relativity, these correspond to the speed of light.

Solution 23.6

It is easy to show that the substitutions in Eq. (53) will change Eqs. (52) to

$$\left\{\gamma_\mu\left(p_\mu - \frac{e}{c}A'_\mu\right) + a\gamma_\mu\gamma_\nu F'_{\mu\nu} - imc\right\}\psi' = 0 \tag{101}$$

where

$$F'_{\mu\nu} = \frac{\partial A'_\nu}{\partial x_\mu} - \frac{\partial A'_\nu}{\partial x_\nu}$$

Now

$$\gamma_\mu\gamma_\nu F_{\mu\nu} = 2i(\Sigma \cdot \mathbf{H} - i\alpha \cdot \mathbf{E})$$

where

$$\Sigma = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix}$$

We can now proceed exactly as in Section 23.8 to obtain an equation similar to Eq. (48) with an extra term

$$\left\{ \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A} \right)^2 - \frac{e\hbar}{2mc}\,\boldsymbol{\sigma}\cdot\mathbf{H} - 2ac\,\boldsymbol{\sigma}\cdot\mathbf{H} + e\phi \right\} u = \varepsilon u$$

The constant a can now be adjusted to give the observed value for the anomalous magnetic moment of a particle such as the proton.

Solution 23.7

We have

$$S = 1 + \left(\frac{i\phi}{2}\right)\sigma_{12} + \frac{1}{2!}\left(\frac{i\phi}{2}\right)^2 \sigma_{12}^2 + \dots$$

Now

$$\sigma_{12}^2 = (i)^2\,\gamma_1\gamma_2\gamma_1\gamma_2 = -(-\gamma_1\gamma_2\gamma_2\gamma_1) = +1$$

$$\sigma_{12}^3 = \sigma_{12}\sigma_{12}^2 = \sigma_{12} \text{ etc.}$$

It is easily shown that

$$S = \cos\phi/2 - \gamma_1\gamma_2 \sin\phi/2 \tag{102}$$

We now have to show that

$$S\gamma_\lambda S^{-1} = a_{\lambda\nu}\gamma_\nu \tag{103}$$

or

$$S\gamma_\lambda = a_{\lambda\nu}\gamma_\nu S \tag{104}$$

Here

$$a_{\lambda\nu} = \begin{bmatrix} \cos\phi & \sin\phi & 0 & 0 \\ -\sin\phi & \cos\phi & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

as may be seen from working out the coordinate transformations under the desired rotation

$$x' = ax$$

For $\lambda = 3$ and 4, Eq. (104) merely says that S, γ_l commute. For example, the second term in S [Eq. (102)] gives a term proportional to $\gamma_1\gamma_2\gamma_3 = -\gamma_1\gamma_3\gamma_2 = \gamma_3\gamma_1\gamma_2$. We, therefore, merely have to prove the result for

$\lambda = 1, 2.$ We have (for $\lambda = 1$)

$$S\gamma_1 = \gamma_1 \cos\phi/2 + \gamma_2 \sin\phi/2$$

and

$$a_{1\nu}\gamma_\nu S = (\gamma_1 \cos\phi + \gamma_2 \sin\phi)\, S$$

$$= \gamma_1 \cos\phi \cos\frac{\phi}{2} - \gamma_2 \cos\phi \sin\frac{\phi}{2}$$

$$+ \gamma_2 \sin\phi \cos\frac{\phi}{2} + \gamma_1 \sin\phi \sin\frac{\phi}{2}$$

$$= \gamma_1 \cos\phi/2 + \gamma_2 \sin\phi/2$$

Similarly, we can establish the result for $\lambda = 2$.

Solution 23.8

The Lorentz transformation is defined by

$$a_{\lambda\nu} = \begin{bmatrix} \gamma & 0 & 0 & i\beta\gamma \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -i\beta\gamma & 0 & 0 & \gamma \end{bmatrix} \tag{105}$$

where $\gamma = (1 - \beta^2)^{-1/2}$, not to be confused with the γ matrices. Proceeding as in Problem 23.7, we have

$$S\gamma_1 = \gamma_1 \cos\frac{\phi}{2} + \gamma_4 \sin\frac{\phi}{2}$$

and

$$a_{1\nu}\gamma_\nu S = (\gamma\gamma_1 + i\beta\gamma\gamma_4)\, S$$

$$= \gamma_1\left(\gamma \cos\frac{\phi}{2} + i\beta\gamma \sin\frac{\phi}{2}\right) + \gamma_4\left(i\beta\gamma \cos\frac{\phi}{2} - \gamma \sin\frac{\phi}{2}\right)$$

from which we obtain (equating the two expressions)

$$\cos\phi = \cos\theta = \gamma$$

$$\sin\phi = i \sinh\theta = i\beta\gamma$$

$$(\text{where } \phi = i\theta)$$

Thus $\quad \tanh\theta = \beta$

and

$$S = \cosh\frac{\theta}{2} - i\gamma_1\gamma_4 \sin\frac{\theta}{2} \tag{106}$$

Solution 23.9

From Eq. (106) $\left[\text{using the result } \gamma_1\gamma_4 = \begin{pmatrix} 0 & -i\sigma_x \\ -i\sigma_x & 0 \end{pmatrix}\right]$ it is easy to show that

$$S = \begin{bmatrix} \cosh\theta/2 & 0 & 0 & \sinh\theta/2 \\ 0 & \cosh\theta/2 & \sinh\theta/2 & 0 \\ 0 & \sinh\theta/2 & \cosh\theta/2 & 0 \\ \sinh\theta/2 & 0 & 0 & \cosh\theta/2 \end{bmatrix} \tag{107}$$

Moreover, writing $\tanh\theta = \dfrac{2\tanh\theta/2}{1+\tanh^2\theta/2} = \beta$ and solving for $\tanh\theta/2$ we obtain

$$\tanh\frac{\theta}{2} = \frac{\gamma-1}{\beta\gamma}$$

(It is easy to see that this is the correct one, the other solution has the wrong limit as $\beta \to 0$). Thus we obtain

$$\cosh\frac{\theta}{2} = \frac{\beta\gamma}{\sqrt{2(\gamma-1)}} = \frac{\beta\gamma}{\sqrt{2}}\frac{\sqrt{1+\gamma}}{\sqrt{\gamma^2-1}} = \sqrt{\frac{1+\gamma}{2}}$$

and

$$\sinh\frac{\theta}{2} = \frac{\beta\gamma}{\sqrt{2}}\frac{1}{\sqrt{1+\gamma}} \tag{108}$$

$\psi' = S\psi$ gives

$$\psi_1' = \psi_1\cosh\frac{\theta}{2} + \psi_4\sinh\frac{\theta}{2} \tag{109}$$

From Eqs. (108) and (109) and similar equations for ψ_2', ψ_3' and ψ_4' the four components can be expressed in terms of the velocity. These solutions should be compared with the solutions obtained directly with $p_y = p_z = 0$. We find, for example,

$$\psi_1' = \sqrt{\frac{1+\gamma}{2}}\begin{bmatrix} 1 \\ 0 \\ 0 \\ \beta/(1+\gamma) \end{bmatrix} \tag{110}$$

so that

$$(\psi')\dagger\psi' = \frac{1+\gamma}{2}\left[1 + \frac{\beta^2\gamma^2}{(1+\gamma)^2}\right] = \gamma \tag{111}$$

This result gives a different normalization from the one given in the text. The trouble is that Eq. (111) gives the probability *density* which is not an invariant quantity; the volume element contracts by a factor $1/\gamma$ along the x direction so that the probability itself is invariant. If we wish to keep the normalization covariant, then solutions (110) are the proper solutions. We leave it as an exercise to show that for the solutions (110)

$$\bar{\psi}_1'\psi_1' = 1 \tag{112}$$

APPENDIX A

Derivation of the Rayleigh-Jeans Formula

The Rayleigh-Jeans Formula

$$u_\nu = \frac{8\pi}{c^3} \nu^2 kT \tag{1}$$

can be derived from a variety of arguments. Planck's was a particularly simple one to emphasize the generality of the principles upon which it was based. First, he assumed that the radiators were oscillating charged dipoles and the energy radiated by one such oscillator was, in accordance with classical electrodynamics, given by*

$$\left|\frac{dW}{dt}\right|_{\text{emission}} = \frac{2}{3}\,\frac{e^2}{mc^3}\,(2\pi\nu)^2\bar{\varepsilon} \tag{2}$$

Here e is the charge, m is the mass of the electron, c the speed of light in free space and $\bar{\varepsilon}$ the average energy of the oscillator. On the other hand, when matter and radiation are in equilibrium, this must equal the energy absorbed per second, i.e., the rate of work done on the oscillator by radiation. Planck showed that this was simply

$$\left|\frac{dW}{dt}\right|_{\text{absorption}} = \frac{\pi e^2}{3m}\,u_\nu \tag{3}$$

Equating (2) and (3), one obtains the Rayleigh-Jeans formula, Eq. (1), if the average energy $\bar{\varepsilon}$ is taken to be kT.

Alternatively, by considering the radiation field inside a cubical cavity, we may write

$u_\nu\, d\nu$ = (Number of modes/unit volume in the frequency interval $d\nu$) × (energy associated with a mode)

$$= \frac{8\pi\,\nu^2\,d\nu}{c^3} \times kT$$

where we have used Eq. (13) of Appendix M.

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*Both Eqs. (2) and (3) are derived in Born (1962) Chapter VII.

APPENDIX B

Average Energy of Planck's Oscillators

In this appendix we will evaluate the summations appearing in Eq. (3) of Chapter 1. We rewrite the equation as

$$\bar{\varepsilon} = \frac{kT \sum_{n=0}^{\infty} nx\, e^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}} \tag{1}$$

where $x = h\nu/kT$. Now $\sum_{n=0}^{\infty} e^{-nx}$ is a geometric series and it is easily shown that

$$\sum_{n=0}^{\infty} e^{-nx} = \frac{1}{1 - e^{-x}} \tag{2}$$

Differentiating Eq. (2) with respect to x, one obtains

$$\sum_{n=0}^{\infty} ne^{-nx} = \frac{e^{-x}}{(1 - e^{-x})^2} \tag{3}$$

Thus

$$\bar{\varepsilon} = \frac{kT\,x\, e^{-x}}{(1 - e^{-x})} = \frac{h\nu}{e^{h\nu/kT} - 1} \tag{4}$$

APPENDIX C

The Equation of Continuity

In this appendix we will derive the equation of continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J} = 0 \tag{1}$$

where ρ represents the number of particles per unit volume and $\mathbf{J}$ the current density; we are assuming that there are no sources or sinks. We consider an infinitesimal volume $dx\,dy\,dz$ as shown in Fig. C.1. The number of particles entering the volume through ABCD (whose area is $dy\,dz$) per unit time is $J_x(x, y, z)\,dy\,dz$; similarly, the number of particles leaving the volume through EFGH per unit time is $J_x(x + dx, y, z)\,dy\,dz$. Thus the net influx per unit time through the two surfaces is

$$\begin{aligned} J_x(x, y, z)\,dy\,dz &- J_x(x + dx, y, z)\,dy\,dz \\ &= -\frac{\partial J_x}{\partial x}\,dx\,dy\,dz \end{aligned} \tag{2}$$

We can similarly calculate the net influx per unit time through the other four surfaces. The total net influx per unit time would be

$$-\left(\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}\right) dx\,dy\,dz = -\nabla \cdot \mathbf{J}\,dx\,dy\,dz \tag{3}$$

Now, the number of particles in the volume element is $\rho\,dx\,dy\,dz$, thus

$$\frac{\partial \rho}{\partial t}\,dx\,dy\,dz = -(\nabla \cdot \mathbf{J})\,dx\,dy\,dz$$

from which we immediately obtain Eq. (1) which is known as the equation of continuity.

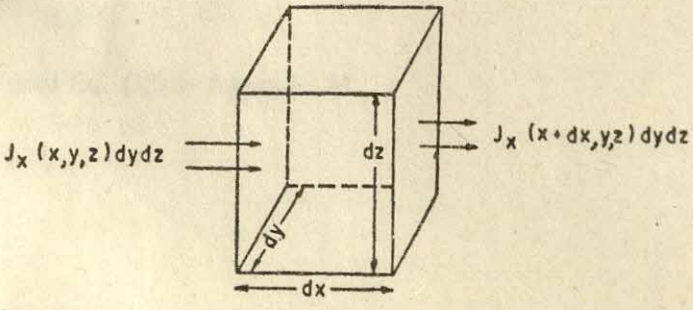

Fig. C. 1 The transport of particles through the surfaces ABCD and EFGH

APPENDIX D

The Fourier Series and the Fourier Transform

According to Fourier's theorem, a periodic function with period α, i.e.,

$$f(x + n\alpha) = f(x)\,, \quad n = 0, \pm 1, \pm 2, \ldots \tag{1}$$

can be expanded in the form

$$f(x) = \frac{1}{2} a_0 + \sum_{n=1}^{\infty} \left[a_n \cos\left(\frac{2\pi\, nx}{\alpha}\right) + b_n \sin\left(\frac{2\pi\, nx}{\alpha}\right) \right] \tag{2}$$

The coefficients a_n and b_n can easily be determined by using the following properties of the trigonometric functions :

$$\frac{2}{\alpha} \int_{x_0}^{x_0+\alpha} \cos\left(\frac{2\pi\, nx}{\alpha}\right) \cos\left(\frac{2\pi\, mx}{\alpha}\right) dx = \delta_{mn} \tag{3}$$

$$\frac{2}{\alpha} \int_{x_0}^{x_0+\alpha} \sin\left(\frac{2\pi\, nx}{\alpha}\right) \sin\left(\frac{2\pi\, mx}{\alpha}\right) dx = \delta_{mn} \tag{4}$$

$$\frac{2}{\alpha} \int_{x_0}^{x_0+\alpha} \sin\left(\frac{2\pi\, nx}{\alpha}\right) \cos\left(\frac{2\pi\, mx}{\alpha}\right) dx = 0 \tag{5}$$

where x_0 is arbitrary and δ_{nm} is the Kronecker delta function defined through the following equation

$$\delta_{mn} = \begin{cases} 0 & \text{if } m \neq n \\ 1 & \text{if } m = n \end{cases} \tag{6}$$

If we multiply Eq. (2) by $\cos(2\pi\, mx/\alpha)$ and integrate from x_0 to $x_0 + \alpha$ and then use Eqs. (3) and (5), we would obtain

$$a_m = \frac{2}{\alpha} \int_{x_0}^{x_0+\alpha} f(x) \cos\left(\frac{2\pi\, mx}{\alpha}\right) dx; \quad m = 0, 1, 2, \ldots \tag{7}$$

Similarly

$$b_m = \frac{2}{\alpha} \int_{x_0}^{x_0+\alpha} f(x) \sin\left(\frac{2\pi\, mx}{\alpha}\right) dx; \quad m = 1, 2, \ldots \tag{8}$$

For the sake of convenience we choose $x_0 = -\alpha/2$. If we now substitute the above expressions in Eq. (2), we would obtain

$$f(x) = \frac{1}{\alpha} \int_{-\alpha/2}^{+\alpha/2} f(x')\,dx' + \sum_{n=1}^{\infty} \left[\frac{2}{\alpha} \cos\left(\frac{2\pi\, nx}{\alpha}\right) \int_{-\alpha/2}^{+\alpha/2} f(x') \cos\left(\frac{2\pi\, nx'}{\alpha}\right) dx' \right.$$
$$\left. + \frac{2}{\alpha} \sin\left(\frac{2\pi\, nx}{\alpha}\right) \int_{-\alpha/2}^{\alpha/2} f(x') \sin\left(\frac{2\pi\, nx'}{\alpha}\right) dx' \right] \tag{9}$$

or

$$f(x) = \frac{\Delta k}{2\pi} \int_{-\pi/\Delta k}^{+\pi/\Delta k} f(x')\,(dx')$$
$$+ \sum_{n=1}^{\infty} \left[\frac{\Delta k}{\pi} \int_{-\pi/\Delta k}^{+\pi/\Delta k} f(x') \cos\,[n\,\Delta k\,(x' - x)]\,dx' \right] \tag{10}$$

where

$$\Delta k = \frac{2\pi}{\alpha} \tag{11}$$

We now let $\alpha \rightarrow \infty$ so that $\Delta k \rightarrow 0$. Thus, if the integral

$$\int_{-\infty}^{+\infty} | f(x') |\, dx'$$

exists (i.e., if it has a finite value), then the first term on the right hand side of Eq. (10) would go to zero. Further, since

$$\int_{0}^{\infty} F(k)\,dk = \underset{\Delta k \rightarrow 0}{\text{Lt}} \sum_{n=1}^{\infty} F\,(n\,\Delta k)\,\Delta k \tag{12}$$

we have, in the limit $\Delta k \rightarrow 0$,

$$f(x) = \frac{1}{\pi} \int_{0}^{\infty} \left\{ \int_{-\infty}^{+\infty} f(x') \cos\,[k(x' - x)]\,dx' \right\} dk \tag{13}$$

The above equation is known as the Fourier Integral. Since the cosine function inside the integral is an even function of k, we may write

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left\{ \int_{-\infty}^{\infty} f(x') \cos\,[k(x' - x)]\,dx' \right\} dk \tag{14}$$

Further, since $\sin\,[k(x' - x)]$ is an odd function of k,

$$0 = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left\{ \int_{-\infty}^{+\infty} f(x') \sin\,[k(x' - x)]\,dx' \right\} dk \tag{15}$$

Adding (or subtracting) Eqs. (14) and (15), we get

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \int_{-\infty}^{\infty} f(x') \exp\left[\pm ik(x' - x)\right] dx'\, dk \tag{16}$$

Thus, if

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x')\, e^{-ikx'}\, dx' \tag{17}$$

then

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k)\, e^{+ikx}\, dk \tag{18}$$

The function $F(k)$ is known as the Fourier transform of $f(x)$ and conversely. As an example, if we assume

$$f(x) = A\, e^{-x^2/2\sigma^2}\, e^{+ik_0x} \tag{19}$$

then straightforward integrations will give (see Eq. 8 of Appendix E).

$$F(k) = A\sigma \exp\left[-\frac{(k - k_0)^2\, \sigma^2}{2}\right] \tag{20}$$

Equations (19) and (20) tell us the general rule that if a function is localized within a distance $\Delta x \sim \sigma$ then its Fourier transform is localized in $\Delta k \sim 1/\sigma$; thus $\Delta k\, \Delta x \sim 1$. If we use the variable $p = \hbar k$, we may write

$$a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \psi(x')\, e^{-ipx'/\hbar}\, dx' \tag{21}$$

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} a(p)\, e^{ipx/\hbar}\, dp \tag{22}$$

which are the relations used in Chapter 2.

A comparison of Eq. (16) with Eq. (3) of Appendix F gives us

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{\pm ik(x-x')}\, dk = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} e^{\pm ip(x-x')/\hbar}\, dp \tag{23}$$

Finally,

$$\int_{-\infty}^{+\infty} |f(x)|^2\,dx = \int_{-\infty}^{+\infty} dx\,\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} F^*(k)\,e^{-ikx}\,dk$$
$$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} F(k')\,e^{ik'x}\,dk'$$
$$= \int_{-\infty}^{+\infty} dk\,F^*(k)\int_{-\infty}^{+\infty} dk'\,F(k')\,\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-ix(k-k')}\,dx$$
$$= \int_{-\infty}^{+\infty} dk\,F^*(k)\int_{-\infty}^{+\infty} dk'\,F(k')\,\delta\,(k-k')$$
$$= \int_{-\infty}^{+\infty} dk\,|F(k)|^2 \tag{24}$$

which is known as Parseval's theorem. It is readily seen that

$$\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = \int_{-\infty}^{+\infty} |a(p)|^2\,dp \tag{25}$$

A more detailed account of Fourier integrals can be found in Titchmarsh (1948).

APPENDIX E

Gamma Functions and Integrals involving Gaussian Functions

The gamma function is defined through the integral

$$\Gamma(z) = \int_0^\infty x^{z-1} e^{-x}\, dx \quad (\text{Re}\, z > 0) \tag{1}$$

For Re $z > 1$, if we integrate by parts we would obtain

$$\Gamma(z) = (z - 1)\,\Gamma(z) \tag{2}$$

Since

$$\Gamma(1) = \int_0^\infty e^{-x}\, dx = 1$$

we immediately obtain

$$\Gamma(n + 1) = n\,!\,; \qquad n = 0, 1, 2, \ldots \tag{3}$$

Further, as we will show below (see Eq. 6)

$$\Gamma(\tfrac{1}{2}) = \sqrt{\pi} \tag{4}$$

Therefore

$$\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\,\Gamma\left(\frac{1}{2}\right) = \frac{1}{2}\sqrt{\pi}, \qquad \Gamma\left(\frac{5}{2}\right) = \frac{3}{2}\cdot\frac{1}{2}\sqrt{\pi} \text{ etc.} \tag{5}$$

Now, let $I = \int_{-\infty}^{+\infty} e^{-x^2}\, dx$, then

$$I^2 = \int_{-\infty}^{+\infty} e^{-x^2}\, dx \int_{-\infty}^{+\infty} e^{-y^2}\, dy = \iint_{-\infty}^{+\infty} e^{-(x^2+y^2)}\, dx\, dy$$

$$= \int_0^\infty \int_0^{2\pi} e^{-r^2}\, r dr\, d\theta \text{ (changing to polar coordinates)}$$

$$= \pi$$

Thus

$$\sqrt{\pi} = \int_{-\infty}^{+\infty} e^{-x^2}\,dx = 2\int_{0}^{\infty} e^{-x^2}\,dx = \int_{0}^{\infty} t^{-1/2}\,e^{-t}\,dt = \Gamma\left(\frac{1}{2}\right) \tag{6}$$

Further, for $n = 0, 1, 2, \ldots$

$$\int_{-\infty}^{+\infty} x^{2n+1}\,e^{-x^2}\,dx = 0 \qquad \text{(because the integrand is odd)}$$

and

$$\int_{-\infty}^{+\infty} x^{2n}\,e^{-x^2}\,dx = 2\int_{0}^{\infty} x^{2n}\,e^{-x^2}\,dx = \int_{0}^{\infty} t^{n-1/2}\,e^{-t}\,dt$$

$$= \Gamma\left(n + \frac{1}{2}\right) = \frac{1\cdot 3\cdot 5\ldots(2n-1)\sqrt{\pi}}{2^n} \tag{7}$$

Finally, the integral $\int_{-\infty}^{+\infty} \exp\left[-\alpha x^2 + \beta x\right] dx$ can be evaluated by completing the square

$$-\alpha x^2 + \beta x = -\alpha\left[x^2 - \frac{\beta}{\alpha}x + \left(\frac{\beta}{2\alpha}\right)^2 - \left(\frac{\beta}{2\alpha}\right)^2\right]$$

Thus

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2+\beta x}\,dx = e^{\beta^2/4\alpha}\int_{-\infty}^{+\infty} e^{-\alpha t^2}\,dt = \left(\frac{\pi}{\alpha}\right)^{1/2} \exp\left[\frac{\beta^2}{4\pi}\right] \tag{8}$$

(Re $\alpha > 0$, β complex)

APPENDIX F

The Dirac Delta Function

The Dirac delta function is defined through the equations

$$\delta(x-a) = 0 \quad \text{for } x \neq a \tag{1}$$

$$\int_{a-\alpha}^{a+\alpha} \delta(x-a)\,dx = 1, \quad \alpha > 0 \tag{2}$$

Thus at $x = a$, the delta function has an infinite value such that the area under the curve is unity. For an arbitrary function $f(x)$ that is continuous at $x = a$, one obtains

$$\int_{a-\alpha}^{a+\alpha} f(x)\,\delta(x-a)\,dx = f(a) \tag{3}$$

There are many representations of the delta function, e.g., the Gaussian function

$$G_\sigma(x) = \frac{1}{\sigma(2\pi)^{1/2}} \exp\left[-\frac{(x-a)^2}{2\sigma^2}\right] \tag{4}$$

has unit area*, i.e.

$$\int_{-\infty}^{+\infty} G_\sigma(x)\,dx = 1 \tag{5}$$

irrespective of the value of σ. Further, the function $G_\sigma(x)$ has a value $1/\sigma(2\pi)^{1/2}$ at $x = 0$ and has a width $\sim \sigma$. Thus, in the limit of $\sigma \to 0$, it has all the properties of the delta function (see Fig. F.1) and we may write

$$\delta(x-a) = \underset{\sigma\to 0}{\mathrm{Lt}} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-a)^2}{2\sigma^2}\right] \tag{6}$$

Similarly, one can show that for a large value of g the function $\sin g(x-a)/\pi(x-a)$ is sharply peaked around $x = a$ (see Fig. F.2) and has a unit area irrespective of the value of g. Thus we may write**

$$\delta(x-a) = \underset{g\to\infty}{\mathrm{Lt}} \frac{\sin g(x-a)}{\pi(x-a)} \tag{7}$$

---

*The integral in Eq. (5) can be easily evaluated by using results of Appendix E.

**In a similar manner, one can show that

$$\delta(x-a) = \underset{g\to\infty}{\mathrm{Lt}} \frac{1}{\pi g} \frac{\sin^2 g(x-a)}{(x-a)^2}$$

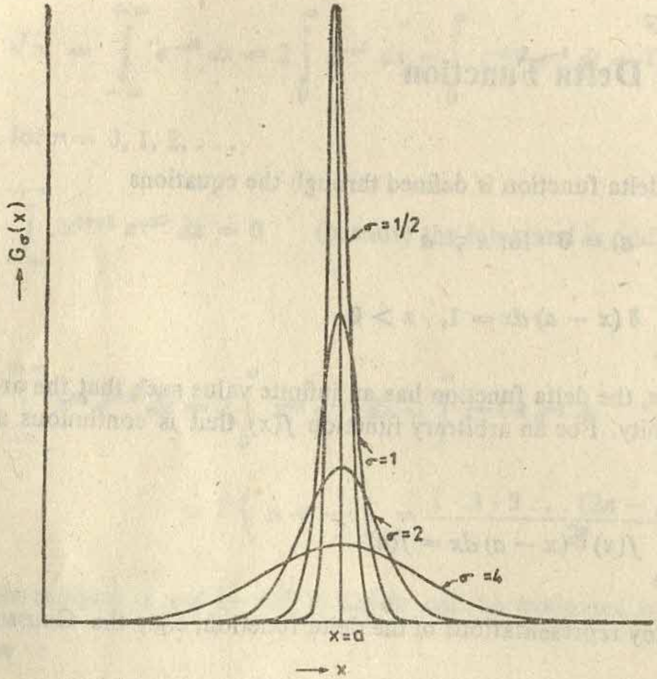

Fig. F.1 In the limit of $\sigma \to 0$, the Gaussian function $G_\sigma(x)$ tends to a delta function

Since

$$\frac{1}{2\pi}\int_{-g}^{g} e^{\pm ik(x-a)}\,dk = \frac{\sin g(x-a)}{\pi(x-a)} \tag{8}$$

we obtain another representation for the delta function (see also Eq. 16 of Appendix D)

$$\delta(x-a) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{\pm ik(x-a)}\,dk = \int_{-\infty}^{+\infty} e^{\pm i2\pi u(x-a)}\,du \tag{9}$$

where $u = k/2\pi$. It can be easily seen that

$$\delta(x-a) = \delta(a-x) \tag{10}$$

$$\delta\left[\,p\,(x-a)\,\right] = \frac{1}{|\,p\,|}\,\delta(x-a) \tag{11}$$

$$\int_{-\infty}^{+\infty} \delta(x-a)\,\delta\,(x-b)\,dx = \delta(a-b) \tag{12}$$

$$f(x)\,\delta\,(x-a) = f(a)\,\delta\,(x-a) \tag{13}$$

$$\delta(x^2-a^2) = \frac{1}{2a}\,[\delta(x-a)+\delta(x+a)],\quad a>0 \tag{14}$$

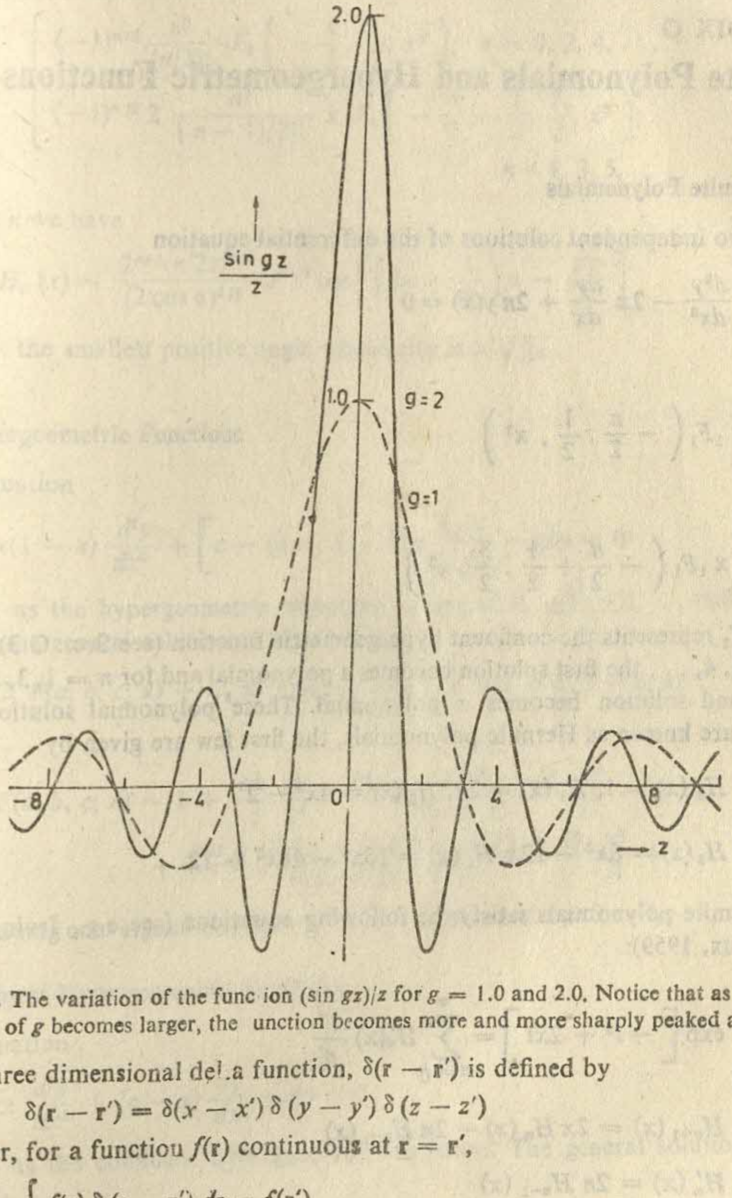

Fig. F.2 The variation of the function $(\sin gz)/z$ for $g = 1.0$ and 2.0. Notice that as the value of g becomes larger, the function becomes more and more sharply peaked at $z = 0$

The three dimensional delta function, $\delta(\mathbf{r} - \mathbf{r}')$ is defined by

$$\delta(\mathbf{r} - \mathbf{r}') = \delta(x - x')\,\delta(y - y')\,\delta(z - z') \tag{15}$$

Further, for a function $f(\mathbf{r})$ continuous at $\mathbf{r} = \mathbf{r}'$,

$$\int f(\mathbf{r})\,\delta(\mathbf{r} - \mathbf{r}')\,d\mathbf{r} = f(\mathbf{r}') \tag{16}$$

Using Eq. (15) one can write down the various representations of $\delta(\mathbf{r} - \mathbf{r}')$; e.g.,

$$\delta(\mathbf{r} - \mathbf{r}') = \operatorname*{Lt}_{\sigma \to 0} \frac{1}{(2\pi)^{3/2}\sigma^3} \exp\left[-\frac{(x - x')^2 + (y - y')^2 + (z - z')^2}{2\sigma^2} \right] \tag{17}$$

Further

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \iiint_{-\infty}^{\infty} e^{i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}')}\,dk_x\,dk_y\,dk_z \tag{18}$$

APPENDIX G

Hermite Polynomials and Hypergeometric Functions

G.1 Hermite Polynomials

The two independent solutions of the differential equation

$$\frac{d^2y}{dx^2} - 2x\,\frac{dy}{dx} + 2n\,y(x) = 0 \tag{1}$$

are

$$_1F_1\left(-\frac{n}{2}, \frac{1}{2}, x^2\right) \tag{2}$$

and

$$x\,{}_1F_1\left(-\frac{n}{2} + \frac{1}{2}, \frac{3}{2}, x^2\right) \tag{3}$$

where $_1F_1$ represents the confluent hypergeometric function (see Sec. G.3). For $n = 0, 2, 4, \ldots$ the first solution becomes a polynomial and for $n = 1, 3, 5, \ldots$ the second solution becomes a polynomial. These polynomial solutions of Eq. (1) are known as Hermite polynomials, the first few are given by

$$\begin{aligned} &H_0(x) = 1,\ H_1(x) = 2x,\ H_2(x) = 4x^2 - 2 \\ &H_3(x) = 8x^3 - 12x,\ H_4(x) = 16x^4 - 48x^2 + 12 \end{aligned} \tag{4}$$

The Hermite polynomials satisfy the following equations (see, e.g., Irving and Mullineux, 1959):

$$\exp\left[-t^2 + 2xt\right] = \sum_{n=0}^{\infty} H_n(x)\,\frac{t^n}{n!} \tag{5}$$

$$H_{n+1}(x) = 2x\,H_n(x) - 2n\,H_{n-1}(x) \tag{6}$$

$$H_n'(x) = 2n\,H_{n-1}(x) \tag{7}$$

$$\int_{-\infty}^{+\infty} e^{-x^2} H_m(x)\,H_n(x)\,dx = 2^n n!\,\sqrt{\pi}\,\delta_{mn} \tag{8}$$

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n}\left(e^{-x^2}\right) \quad n = 0, 1, 2, \ldots \tag{9}$$

The LHS of Eq. (5) is known as the generating function. Equation (6) is known as the recurrence relation and Eq. (8) is known as the orthonormality condition. In terms of the confluent hypergeometric function we have

$$H_n(x) = \begin{cases} (-1)^{n/2}\dfrac{n!}{(n/2)!}\,{}_1F_1\left(-\dfrac{n}{2}, \dfrac{1}{2}, x^2\right); & n = 0, 2, 4, \ldots \\ (-1)^{n/2}\,2\,\dfrac{n!}{[(n-1)/2]!}\,x\,{}_1F_1\left(-\dfrac{n}{2}+\dfrac{1}{2}, \dfrac{3}{2}, x^2\right); & \\ & n = 1, 3, 5, \ldots \end{cases} \tag{10}$$

For large n we have

$$H_n(x) \sim \frac{2^{n+1}(n/2e)^{n/2}}{(2\cos\alpha)^{1/2}}\, e^{n\alpha^2}\cos\left[\left(2n+\frac{1}{2}\right)\alpha - \frac{n\pi}{2}\right] \tag{11}$$

where α is the smallest positive angle whose sine is $x/\sqrt{2n}$.

G.2 Hypergeometric Functions

The equation

$$x(1-x)\,\frac{d^2y}{dx^2} + \left[c - (a+b+1)\,x\right]\frac{dy}{dx} - aby = 0 \tag{12}$$

is known as the hypergeometric equation. For $c \neq 0, \pm 1, \pm 2, \ldots$ and for $|z| < 1$, the general solution of Eq. (12) is

$$y = C_1\,F(a, b, c; x) + C_2\,x^{1-c}\,F(a-c+1, b-c+1, 2-c; x) \tag{13}$$

where

$$F(a, b, c; x) = 1 + \frac{ab}{c}\,\frac{x}{1!} + \frac{a(a+1)\,b(b+1)}{c(c+1)}\,\frac{x^2}{2!} + \frac{a(a+1)\,(a+2)\,b(b+1)\,(b+2)}{c(c+1)\,(c+2)}\,\frac{x^3}{3!} + \ldots \tag{14}$$

the series being convergent only for $-1 < x < 1$ provided $c \neq 0, -1, -2, \ldots$.

G.3 Confluent Hypergeometric Functions

The equation

$$x\,\frac{d^2y}{dx^2} + (c-x)\,\frac{dy}{dx} - ay = 0 \tag{15}$$

is known as the confluent hypergeometric equation. The general solution of Eq. (15) is

$$y = C_1\,{}_1F_1(a, c; x) + C_2\,x^{1-c}\,{}_1F_1(a-c+1, 2-c, x) \tag{16}$$

where

$${}_1F_1(a, c; x) = 1 + \frac{a}{c}\,\frac{x}{1!} + \frac{a(a+1)}{c(c+1)}\,\frac{x^2}{2!} + \frac{a(a+1)\,(a+2)}{c(c+1)\,(c+2)}\,\frac{x^3}{3!} + \ldots \tag{17}$$

is known as the confluent hypergeometric function. Equation (17) is convergent for all complex values of x provided $c \neq 0, -1, -2, \ldots$. Indeed

$$\lim_{c \to -n} \frac{{}_1F_1(a, c; x)}{\Gamma(c)} = \frac{\Gamma(a+n+1)}{\Gamma(a)} \frac{x^{n+1}}{(n+1)!} \, {}_1F_1(a+n+1, n+2; x) \tag{18}$$

Further, as $|z| \to \infty$ $(a \neq 0, -1, -2, \ldots)$

$$ {}_1F_1(a, c; z) \sim e^{-i\pi a} \frac{\Gamma(c)}{\Gamma(c-a)} z^{-a} + \frac{\Gamma(c)}{\Gamma(a)} e^{z} z^{a-c} \tag{19}$$

(see Appendix K).

APPENDIX H

Bessel Functions and Spherical Bessel Functions

H.1 Bessel Functions

The differential equation

$$x^2 \frac{d^2y}{dx^2} + x \frac{dy}{dx} + (x^2 - n^2)\, y(x) = 0 \tag{1}$$

is known as the Bessel equation. For $n \neq 0, 1, 2, \ldots$ the two linearly independent solutions are

$$J_n(x) \quad \text{and} \quad J_{-n}(x)$$

where

$$J_n(x) = \sum_{r=0}^{\infty} (-1)^r \frac{1}{r!\,\Gamma(n+r+1)} \left(\frac{x}{2}\right)^{n+2r} \tag{2}$$

For $n = 0, 1, 2, \ldots$ $J_{-n}(x)$ is a multiple of $J_n(x)$; indeed

$$J_{-n}(x) = (-1)^n J_n(x)\,; \quad n = 0, 1, 2, \ldots \tag{3}$$

For $n = 0, 1, 2, \ldots$ the other independent solution is

$$Y_n(x) = \operatorname*{Lim}_{\nu \to n} \frac{\cos \nu\pi\, J_\nu(x) - J_{-\nu}(x)}{\sin \nu\pi} \tag{4}$$

In fact $Y_n(x)$ always represents an independent solution*.

For $n = \pm \frac{1}{2}, \pm \frac{3}{2}, \ldots$ the infinite series given by Eq. (2) can be summed** and one has

$$\left.\begin{aligned} J_{1/2}(x) &= \left(\frac{2}{\pi x}\right)^{1/2} \sin x\,, \quad J_{-1/2}(x) = \left(\frac{2}{\pi x}\right)^{1/2} \cos x \\ J_{3/2}(x) &= \left(\frac{2}{\pi x}\right)^{1/2} \left(\frac{\sin x}{x} - \cos x\right), \\ J_{-3/2}(x) &= \left(\frac{2}{\pi x}\right)^{1/2} \left(-\frac{\cos x}{x} - \sin x\right) \end{aligned}\right\} \tag{5}$$

---

*The series representing $Y_n(x)$ is never really needed but is given below for the sake of completeness

$$Y_n(x) = \frac{2}{\pi}\left[\left(\ln \frac{x}{2} + \gamma\right) J_n(x) - \frac{1}{2} \sum_{r=0}^{\infty} \frac{(n-r-1)!}{r!} \left(\frac{x}{2}\right)^{-n+2r}\right.$$

$$\left. - \frac{1}{2} \sum_{r=0}^{\infty} (-1)^r \frac{(x/2)^{n+2r}}{r!(r+n)!} \{\phi(r) + \phi(r+n)\}\right]$$

where $\gamma = \operatorname*{Lt}_{n \to \infty} [1 + 1/2 + 1/3 + \ldots + 1/n - \ln n] \approx 0.5772$, $\phi(r) = 1 + 1/2 + \ldots + 1/r$ with $\phi(0) = 0$

**This can also be seen by using the transformation $w = x^{1/2}\, y(x)$ in Eq. (1), the resulting equation for $n = 1/2$ is $w'' + w(x) = 0$, the solution of which are $\sin x$ and $\cos x$.

$J_{\pm 5/2}(x)$, $J_{\pm 7/2}(x)$, etc. can be found from the reeurrence relation

$$J_{n+1}(x) = \frac{2n}{x} J_n(x) - J_{n-1}(x) \tag{6}$$

The asymptotic forms are

$$\left.\begin{aligned} J_n(x) &\underset{x\to\infty}{\to} \left(\frac{2}{\pi x}\right)^{1/2} \cos\left(x - \frac{n\pi}{2} - \frac{\pi}{4}\right) \\ Y_n(x) &\underset{x\to\infty}{\to} \left(\frac{2}{\pi x}\right)^{1/2} \sin\left(x - \frac{n\pi}{2} - \frac{\pi}{4}\right) \end{aligned}\right\} \tag{7}$$

We would like to introduce the Hankel functions which are often used (as independent solutions of Eq. 1) for their convenient asymptotic forms:

$$H_n^{(1)}(x) = J_n(x) + iY_n(x) \underset{x\to\infty}{\longrightarrow} \left(\frac{2}{\pi x}\right)^{1/2} e^{i\left(x - \frac{n\pi}{2} - \frac{\pi}{4}\right)}$$

$$H_n^{(2)}(x) = J_n(x) - iY_n(x) \underset{x\to\infty}{\longrightarrow} \left(\frac{2}{\pi x}\right)^{1/2} e^{-i\left(x - \frac{n\pi}{2} - \frac{\pi}{4}\right)} \tag{8}$$

H.2 Spherical Bessel Functions

In the Bessel equation [Eq. (1)] corresponding to $n = l + 1/2$ ($l = 0, 1, 2, \ldots$) if we make the transformation $f(x) = y(x)/\sqrt{x}$ we would obtain

$$\frac{d^2f}{dx^2} + \frac{2}{x}\frac{df}{dx} + \left[1 - \frac{l(l+1)}{x^2}\right] f(x) = 0 \tag{9}$$

which is known as the spherical Bessel equation. Equation (9) is of the same form as the radial part of the Schrödinger equation [Eq. (19) of Chapter 5] with $V(r) = 0$ and $x = (2mE/\hbar^2)^{1/2}\, r$. For $l = 0, 1, 2, \ldots$ the twoindependent solutions are known as the spherical Bessel functions and are defined through the following equations

$$j_l(x) = \left(\frac{\pi}{2x}\right)^{1/2} J_{l+1/2}(x)$$

and

$$n_l(x) = (-1)^l \left(\frac{\pi}{2x}\right)^{1/2} J_{-l-1/2}(x) \tag{10}$$

Using the results given in the previous section it is easy to show that

$$j_0(x) = \frac{\sin x}{x}, \quad j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}$$

$$n_0(x) = \frac{\cos x}{x}, \quad n_1(x) = \frac{\cos x}{x^2} + \frac{\sin x}{x} \text{ etc.} \tag{11}$$

$j_2(x)$, $n_2(x)$, etc. can be obtained from the recurrence relation [see Eq. (6)]. Further, the asymptotic forms are

$$j_l(x) \underset{x\to\infty}{\to} \frac{1}{x}\sin\left(x - \frac{l\pi}{2}\right)$$

$$n_l(x) \underset{x\to\infty}{\to} \frac{1}{x}\cos\left(x - \frac{l\pi}{2}\right) \tag{12}$$

and

$$j_l(x) \underset{x\to 0}{\to} \frac{x^l}{(2l+1)!!}$$

$$n_l(x) \underset{x\to 0}{\to} \frac{(2l+1)!!}{(2l+1)}\,\frac{1}{x^{l+1}} \tag{13}$$

where $(2l+1)!! = 1\cdot 3\cdot 5.\ldots(2l+1)$. Finally, the function $u(x) = x\,f(x)$ satisfies the equation

$$\frac{d^2u}{dx^2} + \left[1 - \frac{l(l+1)}{x^2}\right]u(x) = 0 \tag{14}$$

which is of the same form as Eq. (21) of Chapter 5 and Eq. (59) of Chapter 19 with $V(r) = 0$ and $x = (2mE/\hbar^2)^{1/2}\, r$. Obviously, the solution of Eq. (14) is given by

$$u(x) = A\,[x\,j_l(x)] + B\,[x\,n_l(x)] \tag{15}$$

H.3 Modified Bessel Functions

In the Bessel equation (Eq. 1) if we make transformation $\xi = -ix$, we would obtain

$$\xi^2\frac{d^2y}{d\xi^2} + \xi\frac{dy}{d\xi} - (\xi^2 + n^2)\,y(\xi) = 0 \tag{16}$$

The solutions are $J_n(i\xi)$ and $Y_n(i\xi)$. For $n \neq 0, 1, 2, \ldots$ the two independent solutions are written as $I_{\pm n}(\xi)$ where

$$I_n(\xi) = i^{-n}\,J_n(i\xi) = \sum_{r=0}^{\infty}\frac{(\xi/2)^{n+2r}}{r!\,\Gamma\,(n+r+1)} \tag{17}$$

The functions $I_n(\xi)$ are known as modified Bessel functions with the asymptotic form

$$I_n(\xi) \underset{\xi\to\infty}{\longrightarrow} \frac{1}{(2\pi\xi)^{1/2}}\,e^{\xi} \tag{18}$$

These functions are not oscillatory in character [cf. Eq. (7)]. Often it is more convenient to choose

$$K_n(x) = \frac{\pi}{2}\,\frac{I_{-n}(x) - I_n(x)}{\sin n\pi} \xrightarrow[x \to \infty]{} \left(\frac{\pi}{2x}\right)^{1/2} e^{-x} \tag{19}$$

as an independent solution. The functions $K_n(x)$ are known as modified Bessel function of the second kind.

H.4 Airy Functions

The solutions of the differential equation

$$\frac{d^2\psi}{dz^2} - z\psi(z) = 0 \tag{20}$$

can be expressed in terms of Bessel functions. A convenient pair of linearly independent solutions are the Airy functions $Ai(z)$ and $Bi(z)$ which are related to the Bessel functions through the following equations

$$Ai(z) = \frac{1}{3}\sqrt{z}\left[I_{-1/3}(\xi) - I_{1/3}(\xi)\right] = \frac{1}{\pi}\sqrt{\frac{z}{3}}\,K_{1/3}(\xi) \tag{21}$$

$$Bi(z) = \sqrt{\frac{z}{3}}\left[I_{-1/3}(\xi) + I_{1/3}(\xi)\right] \tag{22}$$

$$Ai(-z) = \frac{1}{3}\sqrt{z}\left[J_{1/3}(\xi) + J_{-1/3}(\xi)\right] \tag{23}$$

$$Bi(-z) = \sqrt{\frac{z}{3}}\left[J_{-1/3}(\xi) - J_{1/3}(\xi)\right] \tag{24}$$

where $\xi = \frac{2}{3}z^{3/2}$. The asymptotic forms for large z are

$$Ai(z) \rightarrow \frac{1}{2\sqrt{\pi}}\, z^{-1/4} e^{-\xi} \sum_{0}^{\infty} (-1)^k C_k\, \xi^{-k} \tag{25}$$

$$Ai(-z) \rightarrow \frac{1}{\sqrt{\pi}}\, z^{-1/4}\left[\sin\left(\xi + \frac{\pi}{4}\right)\sum_{0}^{\infty}(-1)^k C_{2k}\,\xi^{-2k} - \cos\left(\xi + \frac{\pi}{4}\right)\sum_{0}^{\infty}(-1)^k C_{2k+1}\,\xi^{-2k-1}\right] \tag{26}$$

$$Bi(z) \rightarrow \frac{1}{\sqrt{\pi}}\, z^{-1/4} e^{\xi} \sum_{0}^{\infty} C_k\, \xi^{-k} \tag{27}$$

$$Bi\,(-z) \to \frac{1}{\sqrt{\pi}} z^{-1/4}\Big[\cos\Big(\xi + \frac{\pi}{4}\Big) \sum_{0}^{\infty} (-1)^k C_{2k}\, \xi^{-2k} + \sin\Big(\xi + \frac{\pi}{4}\Big) \sum_{0}^{\infty} (-1)^k C_{2k+1}\, \xi^{-2k-1}\Big] \qquad (28)$$

where

$$C_0 = 1, \quad C_1 = \frac{5}{72}, \ldots$$

$$C_k = \frac{(2k+1)(2k+3)\ldots(6k-1)}{216^k\, k!} \qquad (29)$$

For further details, the reader is referred to Abramowitz and Stegun (1965).

APPENDIX I

The Spherical Harmonics*

In order to define the spherical harmonics it is necessary to introduce the Legendre polynomials and the associated Legendre functions.

I.1 The Legendre Polynomials

The Legendre polynomials, $P_l(x)$, are the polynomial solutions of the equation

$$(1 - x^2)\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + l(l + 1)\,y\,(x) = 0;\quad l = 0, 1, 2, \ldots \tag{1}$$

The first few Legendre polynomials are

$$P_0(x) = 1,\quad P_1(x) = x,\quad P_2(x) = \tfrac{1}{2}(3x^2 - 1) \tag{2}$$

$$P_3(x) = \tfrac{1}{2}(5x^3 - 3x),\quad P_4(x) = \tfrac{1}{8}(35x^4 - 30x^2 + 3)$$

It may be noted that $P_n(x)$ is a polynomial of order n and for n even and odd the polynomial contains even and odd powers respectively. The orthogonality relation is

$$\int_{-1}^{+1} P_l(x)\,P_{l'}(x)\,dx = \frac{2}{2l + 1}\,\delta_{ll'} \tag{3}$$

Higher order Legendre polynomials can be determined from the recurrence relation

$$(l + 1)\,P_{l+1}(x) = (2l + 1)\,x\,P_l(x) - l\,P_{l-1}(x) \tag{4}$$

I.2 The Associated Legendre Functions

The associated Legendre functions are defined through the equation

$$P_l^m(x) = (1 - x^2)^{m/2}\,\frac{d^mP_l(x)}{dx^m};\quad l = 0, 1, 2, \ldots \qquad m = 0, 1, \ldots l \tag{5}$$

and satisfy the differential equation

$$\left[(1 - x^2)\frac{d^2}{dx^2} - 2x\frac{d}{dx} + l(l + 1) - \frac{m^2}{1 - x^2}\right]P_l^m(x) = 0 \tag{6}$$

Since $P_l(x)$ is a polynomial of order l, we must have $m \leqslant l$. Further,

$$P_l^0(x) = P_l(x) \tag{7}$$

---

*Reference : Irving and Mullineux (1959), Abramowitz and Stegun (1965).

The orthogonality and recurrence relations are

$$\int_{-1}^{+1} P_l^m(x)\, P_{l'}^m(x)\, dx = \frac{2}{(2l+1)}\,\frac{(l+m)!}{(l-m)!}\,\delta_{ll'} \tag{8}$$

and

$$(l+1-m)\, P_{l+1}^m(x) = (2l+1)\, x\, P_l^m(x) - (l+m)\, P_{l-1}^m(x) \tag{9}$$

respectively.

I.3 The Spherical Harmonics

The spherical harmonics are defined through the equation

$$Y_{l,m}(\theta,\varphi) = (-1)^m \left[\frac{2l+1}{4\pi}\,\frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta)\, e^{im\varphi};\ m \geqslant 0 \tag{10}$$

$$Y_{l,-m}(\theta,\varphi) = (-1)^m\, Y_{l,-m}^{*}(\theta,\varphi) \tag{11}$$

$$l = 0, 1, 2, \ldots.;\ m = -l, -l+1, \ldots l$$

and satisfy the following differential equation

$$-\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right] Y_{l,m}(\theta,\varphi) = l(l+1)\, Y_{l,m}(\theta,\varphi) \tag{12}$$

The LHS of the above equation is $L^2/\hbar^2$ [see Eq. (22) of Chapter 6]. The first few spherical harmonics are given in Sec. 6.4 and the higher order ones can be calculated using Eqs. (9) and (10). The orthonormality relation is

$$\int_0^{\pi}\int_0^{2\pi} Y_{l',m'}^{*}(\theta,\varphi)\, Y_{l,m}(\theta,\varphi)\, \sin\theta\, d\theta\, d\varphi = \delta_{ll'}\,\delta_{mm'} \tag{13}$$

Further, the following relations are quite often used in quantum mechanics:

$$\cos\theta\, Y_{l,m} = \left\{\left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m} + \left[\frac{(l+m)(l-m)}{(2l+1)(2l-1)}\right]^{1/2} Y_{l-1,m}\right\} \tag{14}$$

and

$$\sin\theta\, Y_{l,m} = \left\{-\left[\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m+1} + \left[\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}\right]^{1/2} Y_{l-1,m+1}\right\} e^{-i\varphi} \tag{15}$$

APPENDIX J

Hydrogen Atom Wavefunctions

For the hydrogenlike atom $V = -Ze^2/r$ (see Sec. 5.3) and the eigenfunctions are

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)\, Y_{lm}(\theta, \varphi) \tag{1}$$

where

$$\begin{aligned} n &= 1, 2, 3, \ldots \\ l &= 0, 1, 2, \ldots n \\ m &= -l, -l+1, \ldots +l \end{aligned} \tag{2}$$

and $Y_{lm}(\theta, \varphi)$ are the spherical harmonics which have been discussed in Appendix I. The normalized radial functions are given by

$$R_{nl}(r) = -\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\,[(n+l)!]^3}\right\}^{1/2} e^{-(1/2)\rho}\, \rho^l\, L_{n+l}^{2l+1}(\rho) \tag{3}$$

where

$$a_0 = \frac{\hbar^2}{\mu e^3}, \quad \rho = \frac{2Z}{na_0}\, r \tag{4}$$

and

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+2l+1} \frac{[(n+l)!]^2\, \rho^k}{(n-l-1-k)!\,(2l+1+k)!\,k!} \tag{5}$$

are known as the associated Laguerre polynomials. It may be noted that ρ depends on n. The orthonormality condition is

$$\int_0^\infty R_{n'l'}(r)\, R_{nl}(r)\, r^2\, dr = \delta_{nn'}\, \delta_{ll'} \tag{6}$$

and first few $R_{nl}(r)$ are given by

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi} \tag{7}$$

$$\left.\begin{aligned} R_{20} &= \frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2}\left(1 - \frac{\xi}{2}\right) \\ R_{21} &= \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/2}\, \xi \end{aligned}\right\} \tag{8}$$

$$\left.\begin{aligned}
R_{30} &= \frac{2}{3\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/3}\left(1-\frac{2\xi}{3}+\frac{2\xi^2}{27}\right)\\
R_{31} &= \frac{8}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/3}\left(\xi-\frac{\xi^2}{6}\right)\\
R_{32} &= \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\xi/3}\xi^2 \text{ etc.}
\end{aligned}\right\} \tag{9}$$

where $\xi = Zr/a_0$. Further

$$\left.\begin{aligned}
\left\langle\frac{1}{r}\right\rangle &= \frac{1}{n^2}\left(\frac{Z}{a_0}\right)\\
\left\langle\frac{1}{r^2}\right\rangle &= \frac{1}{n^3(l+\frac{1}{2})}\left(\frac{Z}{a_0}\right)^2\\
\left\langle\frac{1}{r^3}\right\rangle &= \frac{1}{n^3\, l(l+\frac{1}{2})\,(l+1)}\left(\frac{Z}{a_0}\right)^3\\
\langle r\rangle &= n^2\left[1+\frac{1}{2}\left\{1-\frac{l(l+1)}{n^2}\right\}\right]\frac{a_0}{Z}
\end{aligned}\right\} \tag{10}$$

where

$$\langle r^m\rangle \equiv \int_0^\infty r^m [R_{nl}(r)]^2 r^2\, dr \tag{11}$$

In general, for $p > -2l-3$

$$\frac{p+1}{n^2}\langle r^p\rangle - (2p+1)\frac{a_0}{Z}\langle r^{p-1}\rangle + \frac{p}{4}\Big[(2l+1)^2-p^2\Big]\left(\frac{a_0}{Z}\right)^2\langle r^{p-2}\rangle = 0 \tag{12}$$

The above relation has been derived in Constantinescu and Magyari (1971), Chapter III. We conclude this appendix by noting that

$$L_n^m(\rho) = \frac{d^m}{d\rho^m}\, L_n(\rho) \tag{13}$$

where $L_n(\rho)$ are known as the Laguerre polynomials and are the polynomial solutions of the differential equation

$$\rho\,\frac{d^2y}{d\rho^2} + (1-\rho)\,\frac{dy}{d\rho} + ny(\rho) = 0 \tag{14}$$

Further

$$\frac{(-s)^m\, e^{-\rho s/1-s}}{(1-s)^{m+1}} = \sum_{n=m}^{\infty} L_n^m(\rho)\,\frac{s^n}{n!} \tag{15}$$

Obviously $L_n^0(\rho) = L_n(\rho)$.

APPENDIX K

Asymptotic Series

In order to study the behaviour of various functions for large values of x, it is often convenient to expand them in inverse powers of x:

$$f(x) = \varphi(x) \left[a_0 + \frac{a_1}{x} + \frac{a_2}{x^2} + \ldots \right] \tag{1}$$

where $\varphi(x)$ is a known function whose behaviour for large x is known. The series, which is often divergent, is usually of great practical importance not only for a qualitative understanding of a function, but even in its computation for large values of x.

K.1 Definition

The series $a_0 + (a_1/x) + (a_2/x^2) + \ldots$ is said to represent $f(x)/\varphi(x)$ *asymptotically*, if

$$\lim_{x \to \pm\infty} \left\{ x^N \left[\frac{f(x)}{\varphi(x)} - \sum_{n=0}^{N} \frac{a_n}{x^n} \right] \right\} \to 0 \tag{2}$$

i.e. for a given value of N, the first N terms of the series can be made as close as may be desired to the ratio $f(x)/\varphi(x)$ by making x large enough. When the series diverges, there will be an *optimal* number of terms of the series to be used to represent $f(x)/\varphi(x)$ for a given x; and therefore, there will be an *unavoidable error*. This *unavoidable error* would decrease as $| x |$ increases. We will now consider a few examples:

Example 1 : Consider the exponential integral

$$f(x) = \int_x^\infty \frac{e^{-y}}{y} \, dy$$

Integrating by parts

$$f(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-y}}{y^2} \, dy$$

$$= \frac{e^{-x}}{x} - \frac{e^{-x}}{x^2} + 2 \int_x^\infty \frac{e^{-y}}{y^3} \, dy$$

Continuing this procedure, we get

$$f(x) = \frac{e^{-x}}{x}\left[1 - \frac{1}{x} + \frac{2!}{x^2} - \frac{3!}{x^3} + \ldots + \frac{(-1)^n\, n!}{x^n}\right]$$

$$+ (-1)^{n+1}(n+1)! \int_x^\infty \frac{e^{-y}}{y^{n+2}}\, dy$$

Thus, in this problem $\varphi(x) = e^{-x}/x$; $a_0 = 1, a_1 = -1, \ldots a_n = (-1)^n n!$. The limit of the ratio of two successive terms of the series is given by

$$\lim_{n\to\infty} \left|\frac{T_{n+1}}{T_n}\right| = \lim_{n\to\infty} \frac{n}{x} \to \infty$$

Thus, the series diverges. Further, the two successive terms become equal in magnitude for $n = x$, indicating that the optimum number of terms for a given x is roughly the integer closset to x.

Typically, for $x = 4$, the exact value of $xe^{+x} f(x) \mid_{x=4} = 0.82533$. However the sum of the series including the 1st, 2nd, 3rd, 4th, 5th, 6th, 7th, 8th and 9th term in the series are 1.00000, 0.75000, 0.87500, 0.78125, 0.87500, 0.75781, 0.93360, 0.62347 and 1.24373 respectively. Thus the optimal value is 0.78125 which occurs at $N = 3$ and $0.82533 - 0.78125$ is the unavoidable error. Further, by taking a large number of terms the accuracy becomes poorer.

Example 2: In a similar manner, one may discuss the asymptotic series of the error function,

$$\text{erfc}\, x = 1 - \text{erf}\, x = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-y^2}\, dy$$

$$= \frac{1}{\sqrt{\pi}} e^{-x^2}\left(\frac{1}{x} - \frac{1}{2x^3} + \frac{1\cdot 3}{2^2 x^5} - \frac{1\cdot 3\cdot 5}{2^3 x^7} + \ldots\right)$$

Example 3: Finally, we will consider the asymptotic form of the solutions of the confluent hypergeometric equation:

$$x\frac{d^2y}{dx^2} + (c - x)\frac{dy}{dx} - ay = 0$$

We substitute the series

$$y = e^{mx} \sum_{r=0}^{\infty} a_r x^{-s-r}$$

On substitution and equating the highest power of x we obtain

$$m = 0 \quad \text{or} \quad m = 1$$

(i) For $m = 0$, $s = a$, $a_1 = -a(a-c+1)\,a_0$, etc. giving

$$y = a_0\,x^{-a}\left[1 - \frac{a(a-c+1)}{1!x} + \frac{a(a+1)(a-c+1)(a-c+2)}{2!x^2}\cdots\right]$$

(ii) For $m = 1$, $s = c - a$, $a_1 = (c-a)(1-a)\,a_0$, etc. giving

$$y = a_0 e^x x^{a-c}\left[1 + \frac{(c-a)(1-a)}{1!x} + \frac{(c-a)(c-a+1)(1-a)(2-a)}{2!x^2}\cdots\right]$$

The asymptotic form of ${}_1F_1\,(a, c, x)$ is a linear combination of the above solutions.

APPENDIX L

Complex Variables

L.1 Complex Integrations

In the theory of functions of a complex variable there is a famous theorem due to Cauchy which states that, if $f(z)$ is an analytic function of z in a certain region around a point $z = a$, then

$$\int_C f(z)\,dz = 0 \tag{1}$$

and

$$\frac{1}{2\pi i}\int_C \frac{f(z)}{z-a}\,dz = f(a) \tag{2}$$

where C is a closed contour taken around $z = a$ in a counter clockwise direction (Fig. L.1). If $f(z)$ can be expanded around $z = z_0$ in the form

$$f(z) = \frac{a_{-m}}{(z-z_0)^m} + \frac{a_{-m+1}}{(z-z_0)^{m-1}} + \dots + \frac{a_{-1}}{z-z_0} + a_0 + a_1(z-z_0) + \dots \tag{3}$$

where m is a *finite* integer, then it can be shown that

$$\frac{1}{2\pi i}\int_C f(z)dz = a_{-1} \tag{4}$$

where C is a contour around $z = z_0$ in the counter-clockwise direction. Note that in Eqs. (3) and (4), $f(z)$ is *not* analytic at $z = z_0$; $f(z)$ has a pole of order m. If $m = 1$, the pole is said to be a simple pole.

The coefficient a_{-1} in the expansion (3) is called the residue of the function $f(z)$. If the pole at $z = z_0$ is a simple pole, then

$$[(z-z_0)\,f(z)]_{z=z_0} = a_{-1} \tag{5}$$

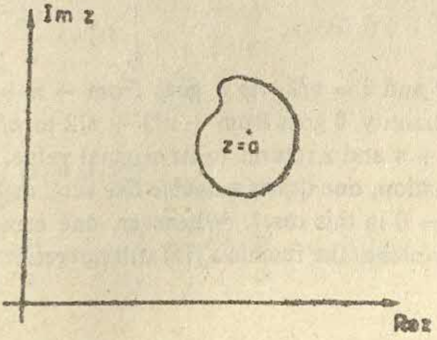

Fig. L.1

Eq. (5) is the recipe for evaluating at simple poles. When there are n poles within a contour C, we can generalize (4) to

$$\frac{1}{2\pi i}\int_C f(z)\,dz = \sum_{r=1}^{n} \alpha_r \tag{6}$$

where α_r is the residue at the rth pole.

Eq. (6) remains unaltered, no matter how we distort the contour C as *long as we do not cross any new poles.* This technique is exploited frequently in mathematical manipulations.

A remarkable property of an analytic function $f(z)$ is that all its derivatives are also analytic in the same region. It can be shown that Eq. (2) can be generalized to

$$f^n(a) = \frac{n!}{2\pi i}\int_C \frac{f(z)dz}{(z-a)^{n+1}} \tag{7}$$

L.2 Singularities

A function $f(z)$ which can be expanded with $m \leqslant -1$ *but finite* is said to have a singularity at $z = z_0$.

It may turn out that an expansion of the form (3) is not possible for *finite m.* For example

$$f(z) = e^{1/z} = \sum_{m=0}^{\infty} \frac{z^{-m}}{m!}$$

In this case the function $f(z)$ is said to have an *essential* singularity at $z = 0$.

One should not get the idea that a singularity is merely a point at which the function goes to infinity. For example, $f(z) = z^{1/2}$ *cannot* be expanded near $z = 0$ in the form (3). Such singularities arise when we have multivalued functions and are called branch points.

L.3 Multivalued Functions

We discuss the example

$$f(z) = z^{1/2} \tag{8}$$

Writing $z = re^{i\varphi}$

and $f(z) = Re^{i\theta}$

we see that $R = r^{1/2}$ and $\theta = \varphi/2$. As φ goes from $-\pi + \varepsilon$ to $\pi - \varepsilon$ where ε is a small positive quantity, θ goes from $-\pi/2 + \varepsilon/2$ to $\pi/2 - \varepsilon/2$. As $\varepsilon \to 0$, φ goes from $-\pi$ to $+\pi$ and z returns to its original value. *However f does not.* To describe this situation, one draws a *double line* such as I (Fig. L.2), around the branch point ($z = 0$ in this case). Whenever, one crosses this line (called *branch line*) on the z-plane, the function $f(z)$ will not return to its original value.

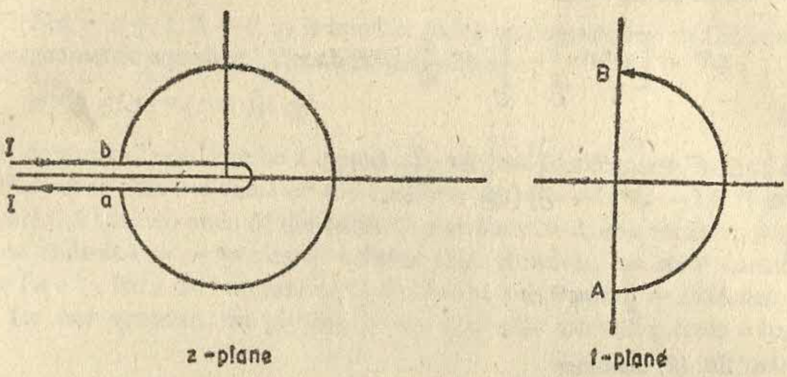

Fig. L.2

It can be shown that branch points, occur in pairs and a branch line joins a pair of branch points. In the above example, $z = \infty$ is the other branch point.

L.4 Application to Solution of Confluent Hypergeometric Equation

We apply the methods of contour integrals to solve the confluent hypergeometric equation.

$$zF'' + (c - z)F' - aF = 0 \tag{9}$$

This equation is of great importance in quantum mechanical problems, since many equations such as Hermite's equation, Legendre and associated Legendre equation and Bessel's equation can be converted to this form. We write tentatively, its solution as $F(a, c, z)$. The method employed it to take the Laplace transform

$$F = \int_C e^{zt} v(t)\, dt \tag{10}$$

where C is a contour in the complex t plane and $v(t)$ a function to be chosen so as to give a solution of Eq. (9) with the desired behaviour. We note that

$$F'(z) = \int_C te^{zt} v(t)\, dt$$

$$= \left[\frac{e^{zt}}{z}\, t\, v(t)\right]_C - \int_C \frac{e^{zt}}{z} \frac{d}{dt}\left[t\, v(t)\right] dt$$

and

$$F''(z) = \int_C t^2 e^{zt} v(t)\, dt$$

$$= \left[\frac{e^{zt}}{z}\, t^2 v(t)\right]_C - \int_C \frac{e^{zt}}{z} \frac{d}{dt}\left[t^2 v(t)\right] dt$$

This permits us to write

$$zF'' = \Big[e^{zt}\,t^2 v\Big]_C - \int_C e^{zt}\,\frac{d}{dt}\,[t^2 v]\,dt$$

$$zF' = \Big[e^{zt}\,tv\Big]_C - \int_C e^{zt}\,\frac{d}{dt}\,[tv]\,dt$$

and

$$cF' = \int_C ct\,ve^{zt}\,dt$$

so that Eq. (9) becomes

$$\Big[e^{zt}\,t(t-1)v(t)\Big]_C - \int_C e^{zt}\left[t^2\,\frac{dv}{dt} + 2tv - t\,\frac{dv}{dt} - v - ct\,v + av\right]dt = 0 \tag{11}$$

We now make the restriction that the contour C will be so chosen that

$$[e^{zt}\,t(t-1)\,v(t)]_C = 0 \tag{12}$$

and the function $v(t)$ will be chosen so that the integrand in (11) vanishes; i.e.

$$\frac{dv}{dt}\,t\,(t-1) = v\,[1-a+(c-2)\,t] \tag{13}$$

Eq. (13) is readily integrated* to give

$$v \sim t^{a-1}\,(t-1)^{c-a-1}$$

and the condition for the contour, Eq. (12), becomes

$$[\phi(t)]_C = [e^{zt}\,t^a\,(t-1)^{c-a}]_C = 0 \tag{14}$$

The solution is [from Eq. (10)]

$$F = \int_C e^{zt}\,t^{a-1}\,(t-1)^{c-a-1}\,dt \tag{15}$$

Before we proceed further, we note that if one substitutes

$$F = z^{1-c}\,F_1 \tag{16}$$

into Eq. (9), we obtain

$$zF_1'' + (2-c-z)\,F_1' - (a-c+1)\,F_1 = 0 \tag{17}$$

which is of the same form as (9). Thus, if we write the solution of (9) in the form

$$F = F\,(a, c, z)$$

---

*This is the point of the whole exercise; the equation in v is simpler than the original one in F.

then $z^{1-c}\, F(a-c+1, 2-c, z)$ is another independent solution of the confluent hypergeometric equation. Thus this solution is

$$z^{1-c} \int e^{zt}\, t^{a-c}\, (t-1)^{c}\, dt \tag{18}$$

Now the contour C need not be a closed one; all that is necessary is that Eq. (14) is obeyed so that the value of the function $\phi(t)\ [= e^{zt}\, t^{a}\, (t-1)^{c-a}]$ must be the same at the two ends of the curve C. For $\operatorname{Re} z > 0$, any contour which starts and ends at $t = -\infty$ clearly satisfies this. However, we shall consider the case $\operatorname{Re} c > \operatorname{Re} a > 0$ so that $\phi(t)$ vanishes at $t = 0$ and $t = 1$. Hence we choose, for our contour, the portion of the real axis extending from 0 to 1. Thus

$$F = \int_0^1 e^{zt}\, t^{a-1}\, (t-1)^{c-a-1}\, dt \tag{19}$$

$$= (-1)^{c-a-1} \sum_{n=0}^{\infty} \frac{z^n}{n!} \int_0^1 t^{n+a-1}\, (1-t)^{c-a-1}\, dt$$

This series can be expressed in terms of Γ functions by using the relation

$$\int_0^1 t^{\alpha-1}\, (1-t)^{\beta-1}\, dt = \frac{\Gamma(\alpha)\, \Gamma(\beta)}{\Gamma(\alpha+\beta)} \tag{20}$$

Thus

$$F = (-1)^{c-a-1} \sum_{n} \frac{z^n}{n!}\, \frac{\Gamma(n+a)\, \Gamma(c-a)}{\Gamma(c+n)}$$

The series*

$${}_1F_1\,(a, c, z) = \frac{\Gamma(c)}{\Gamma(a)} \sum_{n=0}^{\infty} \frac{\Gamma(a+n)}{\Gamma(c+n)}\, \frac{z^n}{n!} \tag{21}$$

is called the *confluent hypergeometric* series. Further

$$F = (-1)^{a-c-1}\, \frac{\Gamma(c-a)\, \Gamma(a)}{\Gamma(c)}\; {}_1F_1\,(a, c, z) \tag{22}$$

A general solution of the hypergeometric equation can, therefore, be expressed as a linear combination of

$${}_1F_1\,(a, c, z) \quad \text{and} \quad z^{1-c}\; {}_1F_1\,(a-c+1, 2-c, z)$$

---

*The peculiar notation ${}_1F_1$ is because this is a special form of generalized hypergeometric function ${}_nF_m\,(a,c,z)$.

L.5 Asymptotic Behaviour

The function (21), written out in a series as

$$ {}_1F_1(a, c, z) = 1 + \frac{a}{c} z + \frac{a(a+1)}{c(c+1)} \frac{z^2}{2!} + \ldots \tag{23} $$

is convergent for all finite values of $|z|$; the only restriction is that c is not a negative integer. We now study the behaviour of this series for large values of $|z|$ when a and c are integers. In this series, the term containing z^n is

$$ \frac{(a+n)!}{(a-1)!} \frac{(c-1)!}{(c+n)!} \frac{z^n}{n!} $$

For large $n \gg a, c$ we have

$$ \frac{(a+n)!}{(c+n)!} \sim n^{a-c} \sim n(n-1)\ldots(n-a+c+1) $$

This gives, for the term with z^n,

$$ \frac{(c-1)!}{(a-1)!} \frac{n^{a-c}}{n!} z^n \approx \frac{(c-1)!}{(a-1)!} \frac{z^n}{(n-a+c)!} $$

Thus, for $z \to \infty$, we have

$$ {}_1F_1 \sim \frac{(c-1)!}{(a-1)!} \sum_n \frac{z^n}{(n-a+c)!} = \frac{(c-1)!}{(a-1)!} z^{a-c} e^z $$

Thus

$$ {}_1F_1(a, c, z) \xrightarrow[z \to \infty]{} \frac{\Gamma(c)}{\Gamma(a)} z^{a-c} e^z \tag{24} $$

We have put the result in terms of the Γ functions because the result it turns out, is valid for non-integral values of a and c as well. While (24) gives the right asymptotic behviour for $\text{Re } z \to \infty$, it can be seen that for $\text{Re } z \to -\infty$, the limit goes to zero exponentially. In this case the limit given by (24) is not valid; however, the following result may be established

$$ {}_1F_1(a, c, z) = e^z {}_1F_1(c-a, c, -z) \tag{25} $$

so that, for $z \to -\infty$, we substitute the asymptotic form (24) on the RHS of Eq. (25), to obtain

$$ {}_1F_1(a, c, z) \xrightarrow[z \to \infty]{} \frac{\Gamma(c)}{\Gamma(c-a)} (-z)^{-a} \tag{25a} $$

L.6 Connection with Other Functions

It can be easily shown that the Hermite polynomial is related to the confluent hypergeometric function. Hermite's equation (see Appendix E) is

$$ \frac{d^2W}{dx^2} - 2x \frac{dW}{dx} + 2n W(x) = 0 $$

For $n = 2m$, we change the variable $x = z^{1/2}$, to obtain

$$zW'' + (\tfrac{1}{2} - z)\, W' + mW = 0$$

For $n = 2m + 1$, the changes

$$x = z^{1/2},\ W = z^{1/2} F$$

give
$$zF'' + (\tfrac{3}{2} - z)\, F' + mF = 0$$

Thus, it can be shown that

$$H_n = (-1)^{\frac{1}{2}n} \frac{n!}{(n/2)!}\, {}_1F_1\left(-\tfrac{1}{2}n, \tfrac{1}{2}, z^2\right) \quad (n \text{ even}) \tag{26}$$

and

$$= 2\,(-1)^{n/2} \frac{n!}{[(n-1)/2]!}\, z\, {}_1F_1\left(\frac{-n+1}{2}, \tfrac{1}{2}, z^2\right) \quad (n \text{ odd}) \tag{27}$$

Since in both cases H_n is related to $F(a, c, z)$ where a is a negative integer (or zero), it is easily seen from (23) that H_n is a polynomial. If this were not the case, as $z \to \infty$, the function H will diverge as e^{z^2}.

Similar arguments lead to the association of the associated Laguerre polynomials

$$L_n^m(z) = \frac{[(m+n)!]^2}{n!\, m!}\, {}_1F_1(-n, m+1, z) \tag{28}$$

where n, m are integers, and of the Bessel functions

$$J_\nu(z) = \frac{z^\nu e^{-iz}}{2^\nu \Gamma(1+\nu)}\, {}_1F_1\left(\nu + \frac{1}{2}, 2\nu + 1, 2iz\right) \tag{29}$$

For $\mathrm{Re}\,(\nu + \frac{1}{2}) > 0$, the following integral representation can be established by the methods discussed:

$$J_\nu(z) = \frac{1}{\sqrt{\pi}\, \Gamma(\nu + \frac{1}{2})} \left(\frac{z}{2}\right)^\nu \int_{-1}^{1} e^{izt} (1 - t^2)^{\nu - 1/2}\, dt$$

APPENDIX M

The Periodic Boundary Conditions and the Density of States

In developing the scattering theory, we consider the particle inside a cube of volume L^3 and initially in a plane wave state corresponding to momentum $\mathbf{p}_i$ (see Sec. 20.3). Thus the particle is described by the wavefunction

$$\psi = \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{1}$$

where

$$\mathbf{k} = \frac{1}{\hbar}\mathbf{p} \tag{2}$$

and the factor $L^{-3/2}$ normalizes the wavefunction

$$\int_0^L\int_0^L\int_0^L |\psi|^2\, dx\, dy\, dz = 1$$

The allowed values of $\mathbf{k}$ are determined from the boundary conditions. It is convenient to use the periodic boundary conditions (see also Sec. 22.3):

$$\begin{aligned}\psi(x=0,y,z) &= \psi(x=L,y,z)\\ \psi(x,y=0,z) &= \psi(x,y=L,z)\end{aligned} \tag{3}$$

and

$$\psi(x,y,z=0) = \psi(x,y,z=L)$$

giving

$$\exp[ik_xL] = 1 = \exp[ik_yL] = \exp[ik_zL] \tag{4}$$

Thus the allowed values of k_x, k_y and k_z are given by [cf. Eq. (37) of Chapter 22]:

$$k_x = \frac{2\pi n_x}{L},\ k_y = \frac{2\pi n_y}{L},\ k_z = \frac{2\pi n_z}{L} \tag{5}$$

where

$$n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots \tag{6}$$

Now, the number of states whose x component of $\mathbf{k}$ lies between k_x and $k_x + dk_x$ would simply be the number of integers lying between $L\,k_x/2\pi$ and $L\,(k_x + dk_x)/2\pi$; this number would be approximately equal to $L\,dk_x/2\pi$. Similarly, the number of states whose y and z components of $\mathbf{k}$ lie between k_y

and $k_y + dk_y$ and k_z and $k_z + dk_z$ would, respectively, be

$$\frac{L}{2\pi}\, dk_y \quad \text{and} \quad \frac{L}{2\pi}\, dk_z$$

Thus there will be

$$\frac{L^3}{8\pi^3}\, dk_x\, dk_y\, dk_z \tag{7}$$

states in the range $dk_x\, dk_y\, dk_z$ of $\mathbf{k}$. Obviously, the number of states in the range $dp_x\, dp_y\, dp_z$ of $\mathbf{p}$ will be

$$\frac{L^3}{8\pi^3 \hbar^3}\, dp_x\, dp_y\, dp_z \tag{8}$$

Now if $\rho(k)\, dk\, d\Omega$ represents the number of states whose $|\mathbf{k}|$ lies between k and $k + dk$ and the direction of $\mathbf{k}$ lies in the solid angle $d\Omega$ ($= \sin\theta\, d\theta\, d\varphi$) then

$$\rho(k)\, dk\, d\Omega = \frac{L^3}{8\pi^3}\, k^2\, dk\, d\Omega \tag{9}$$

For a non-relativistic particle of mass m we have $E = \hbar^2 k^2/2m$ giving

$$\rho(E)\, dE\, d\Omega = \frac{L^3}{16\pi^3 \hbar^3}\, (2m)^{3/2} E^{1/2}\, dE\, d\Omega \tag{10}$$

If we integrate over $d\Omega$ we would get the total number of states whose energies lie between E and $E + dE$

$$g(E)\, dE = \frac{L^3}{4\pi^2 \hbar^3}\, (2m)^{3/2} E^{1/2}\, dE \tag{11}$$

which is identical to the expression for $g(E)$ derived in Problem 5.3 (except for the additional factor of 2 introduced there) where we had assumed end point boundary conditions, i.e., ψ was assumed to vanish on the surface of the cube. Thus the expression for density of states is independent of the boundary conditions used.

Returning to Eq. (9) we note that for an electromagnetic field inside a cube (see Sec. 22.3) $\omega = ck$ and one has

$$\rho(\omega)\, d\omega\, d\Omega = \frac{L^3}{8\pi^3 c^3}\, \omega^2\, d\omega\, d\Omega \tag{12}$$

If we sum over two independent modes of polarization and integrate over the solid angle we would get

$$\rho(\omega)\, d\omega = \frac{L^3}{\pi^2 c^3}\, \omega^2\, d\omega \tag{13}$$

APPENDIX N

Expansion Formula for a Plane Wave

Here we will prove the following formula

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} i^l (2l+1) P_l(\cos\theta)\, j_l(kr) \tag{1}$$

[A more general formula is given by

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-\infty}^{+\infty} i^l j_l(kr)\, Y^*_{lm}(\theta_k, \varphi_k)\, Y_{lm}(\theta_r, \varphi_r) \tag{2}$$

where (θ_k, φ_k) and (θ_r, φ_r) are the polar angles of the vectors **k** and **r** respectively.]

The wave equation for a free particle is

$$\nabla^2\psi + k^2\psi = 0 \tag{3}$$

a solution of which is given by

$$\psi = e^{ikz} = e^{ikr\cos\theta} \tag{4}$$

Equation (3) can also be solved in spherical polar co-ordinates. The solution of Eq. (4) with azimuthal symmetry (i.e., independent of φ) must satisfy

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + k^2\psi = 0 \tag{5}$$

using the method of separation of variables

$$\psi = R(r)\,\Theta(\theta) \tag{6}$$

we get

$$\begin{aligned}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + k^2r^2R(r) &= -\frac{1}{\Theta(\theta)}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\\ &= l(l+1)\quad \text{(say)}\end{aligned} \tag{7}$$

For $\Theta(\theta)$ to be bounded at $\cos\theta = \pm 1$, l must be 0, 1, 2, ... Then the solutions (finite at $r = 0$) are

$$R(r) = j_l(kr)$$

and

$$\Theta(0) = p_l(\mu),\ \mu = \cos\theta$$

Thus any bounded solution of Eq. (3), having azimuthal symmetry can be written as a linear combination of $j_l(kr)\,P_l(\mu)$. Thus

$$e^{i\rho\mu} = \sum_{l=0}^{\infty} a_l j_l(\rho) P_l(\mu); \quad \rho = kr \tag{8}$$

If we multiply both sides by $P_m(\mu)\,d\mu$, integrate and use the orthogonality relation of Legendre polynomials, we get

$$a_m \frac{2}{2m+1} j_m(\rho) = \int_{-1}^{+1} e^{i\rho\mu} P_m(\mu)\,d\mu \tag{9}$$

Equation (9) must be valid for all values of ρ; we take the limit $\rho \to \infty$, then

$$\text{LHS} \sim a_m \frac{2}{2m+1} \frac{1}{\rho} \sin\left(\rho - \frac{m\pi}{2}\right) \tag{10}$$

$$\text{RHS} = \frac{2i^l}{\rho} \sin\left(\rho - \frac{m\pi}{2}\right) - \frac{1}{i\rho} \int_{-1}^{+1} e^{i\rho\mu} \frac{d}{d\mu} P_m(\mu)\,d\mu$$

[integrating by parts]

Thus

$$\text{RHS} \sim \frac{2}{\rho} i^l \sin\left(\rho - \frac{m\pi}{2}\right) \tag{11}$$

Using Eqs. (10) and (11), we get

$$a_m = (2m+1)\,i^l$$

On substitution in Eq. (8) we get Eq. (1).

APPENDIX O

Asymptotic Form of the Radial Part of the Schrodinger Equation for a Short Range Force

For a spherically symmetric potential, the radial part of the Schrödinger equation can be put in the form [see Eqs. (19) and (21) of Chapter 5 and Eq. (59) of Chapter 19]:

$$\frac{d^2 u_l(r)}{dr^2} + \left[k^2 - U(r) - \frac{l(l+1)}{r^2}\right] u_l(r) = 0 \qquad (1)$$

where $u_l(r) = r R_l(r)$, $k^2 = 2mE/\hbar^2$, $U(r) = 2m\, V(r)/\hbar^2$. In this appendix we will show that for a short range force for which

$$\underset{r\to\infty}{\mathrm{Lt}}\; r V(r) = 0 \qquad (2)$$

the asymptotic form of $u_l(r)$ is $\exp(\pm\, ikr)$.

We first assume that at large values of r, the terms $U(r)$ and $l(l+1)/r^2$ in Eq. (1) can be neglected. Then the solution will be $u_l \sim \exp(\pm\, ikr)$, this suggests that we try a solution of the form

$$u_l(r) = A \exp\left[\int_a^r f(r')\, dr'\right] \exp\,[\pm\, ikr] \qquad (3)$$

If we substitute in Eq. (1), we would obtain

$$\frac{df}{dr} + f^2 \pm 2ik\, f(r) = U(r) + \frac{l(l+1)}{r^2} \equiv W(r) \qquad (4)$$

If $W(r)$ behaves as $e^{-\alpha r}$ for $r \to \infty$ (then l is necessarily zero), $f(r)$ will also behave as $e^{-\alpha r}$ as can be seen by substitution (the term f^2 will be negligible). Consequently the integral $\int_a^r f(r')dr'$ will tend to a constant value and $u_l(r)$ will behave as $\exp(\pm\, ikr)$. On the other hand if $W(r) \sim A'/r^\alpha$ $(\alpha > 0)$ then $f(r) \sim \mp\, A'/2ik\, (1/r^\alpha)$ (the terms involving df/dr and f^2 would be negligible). However, only for $\alpha > 1$, the integral $\int_a^r f(r')dr'$ would tend to a constant value. Indeed for $\alpha = 1$ (i.e., for the Coulomb potential) we will have

$$u_l(r) \sum_{r\to\infty} \exp\left(\pm\, ikr \pm \frac{A'}{2ik} \ln r\right) \qquad (5)$$

Thus the form of $u_l(r)$ for $r \to \infty$ does not approach a definite phase; however, we can still obtain an expression for the scattering cross-section (see Sec. 19.2). Thus, if $\alpha > 1$, the asymptotic form of $u_l(r)$ is indeed of the form of $\exp(\pm\, ikr)$.

APPENDIX P

The Free Particle Green's Function

The free particle Green's function is defined through the equation

$$(\nabla^2 + k^2)\, G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{1}$$

We Fourier analyse G and δ :

$$G(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int g(\mathbf{k}') \exp[i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')]\, d\mathbf{k}' \tag{2}$$

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int \exp[i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')]\, d\mathbf{k}' \tag{3}$$

where we have used Eq. (18) of Appendix *F*. Substituting these in Eq. (1) we get

$$(-k'^2 + k^2)\, g(\mathbf{k}') = 1$$

or

$$g(\mathbf{k}') = -\frac{1}{k'^2 - k^2} \tag{4}$$

Thus

$$G(\mathbf{r} - \mathbf{r}') = -\frac{1}{8\pi^3} \int \frac{1}{k'^2 - k^2} \exp[i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')]\, d\mathbf{k}' \tag{5}$$

which is the same as Eq. (29) of Chapter 19.

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In this completely revised edition, extensive changes have been m[illegible] while retaining the emphasis on the applications. Many new topics [illegible] and applications have been introduced. An outline of these is given below.

*There are now three chapters on the exact solutions of the Schrödinger equation; many illustrative examples have been introduced.

*A new chapter on Vector Spaces has been added.

*There are now two chapters on Angular Momentum; the second one introduces Pauli spin matrices etc.

*The chapter on WKB approximation has been completely rewritten.

*New chapters on Hydrogen and Hydrogen-like Atoms, the Helium Atom and the Exclusion Principle, Many Electron Atoms and Numerical Integration of the Schrödinger Equation have been introduced.

*A new chapter on the Semiclassical Theory of Radiation and the Einstein Coefficients has been included, which is followed by a chapter on Quantum Theory of Radiation.

The Nobel Lectures, introduced in the Second Edition, have been retained. These and some of the new chapters should make the book unique.

Professor A K Ghatak is currently Professor of Physics at the Indian Institute of Technology, Delhi. He obtained his M.Sc. from Delhi University and Ph.D. from Cornell University. Prof. Ghatak has published over 100 research papers. His current interest is in the field of electromagnetic wave propagation, particularly in fibre and integrated optics.

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